AN ABSTRACT OF THE THESIS OF

Mark C. Bos for the degree of Master of Science in Chemistry presented on April 24, 1996.

Title: Part I: Development and Application of an Arsenic Speciation Technique Using Ion-Exchange Solid Phase Extraction Coupled with GFAAS;

Part II: Investigation of Zinc Amalgam as a Reductant

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Two related techniques, based upon ion-exchange solid phase extraction, have been developed for the determination of arsenic speciation. The inorganic arsenic species arsenite (As(III)) and arsenate (As(V)) are separated by anion-exchange and detected with graphite furnace atomic absorption spectrophotometry (GFAAS) with a nickel matrix modifier. The first separation technique, which is based on a published method, utilizes a strong anion-exchange resin in a column format. The method was refined to achieve a cleaner and more rapid separation of the As species. In the second separation technique, the recently available Empore™ anion-extraction disks are used. In both cases, rapid separations of several samples are achieved with the use of a vacuum manifold. The simplicity of the separation techniques allows them to be applied in the field which eliminates potential problems due to sample storage.

In the pH range of most natural water samples (5 - 9), As(III) exists as a neutral species which is not retained by the resin, while As(V) exists as a monovalent or divalent species which are subsequently retained by the resin. The two arsenic species are collected in 3 to 4 fractions with As(III) appearing in the first two fractions. The As(V) species is eluted from the resin with 0.1 M HCl and collected in the last one or two fractions. Percent recoveries for each species range from 94 to 99%. The detection limit for each species with GFAAS is 2 μg/L.

The speciation techniques were used successfully in several applications. First, the resin technique was used to monitor the oxidation of As(III) by O_2, H_2O_2, and δ-MnO_2. The technique was also used to monitor the reduction of As(V) by Fe(II) and in solutions containing combinations of Fe(II), Fe(III), and ascorbic acid. Second, the resin technique was used to monitor the redox behavior of arsenic in soil slurries in bio-reactor systems. Upon spiking the soil slurry to a level of 500 μg/L As(V), 80 to 90% of the As(V) was immediately adsorbed, presumably to hydrous Fe(III) oxides. In general, as conditions became more reducing, total soluble arsenic increased as a result of either abiotic or biotic reduction of the As(V) to the more soluble As(III). Third, the disk technique was applied in the field to determine arsenic speciation in creek water at Sutter Creek, Ca., where homes are built upon a large pile of mine tailings containing arsenic. In the creek water, no As(III) was detected but As(V) was detected at a level of 8 μg/L. Fourth and finally, the resin technique was used to determine arsenic speciation when a sample of the mine tailings was placed in a reactor and combined with a soil slurry thus simulating a flooded condition. As conditions became more reducing, up to 800 μg/L As was detected in solution with As(III) accounting for almost 90% of total soluble species.

Also presented here is an investigation of zinc amalgam as a reducing agent for Cr(III) and selected redox indicators. Zinc amalgam, in a column format, also known as the classic Jones Reductor, provides an efficient means for production of Cr(II) and reduced forms of various redox indicators. Finally, the reduction capabilities of Ti(III) citrate and zinc amalgam were compared.

Part I: Development and Application of an Arsenic Speciation Technique Using Ion-Exchange Solid Phase Extraction Coupled with GFAAS

Part II: Investigation of Zinc Amalgam as a Reductant

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stood by my side through thick and thin.

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Chapter 1
Introduction

Two major topics are discussed in this thesis. The initial and major focus will be on development and application of an arsenic speciation technique. In the second part, the focus will shift towards investigation of zinc amalgam as a reductant and its effectiveness in the reduction of Cr(III) and redox indicators.

Initially discussed in this thesis is the development and application of a technique for arsenic speciation which distinguishes arsenate (As(V)) from arsenite (As(III)). Arsenic is toxic and believed to be carcinogenic (1). Currently arsenic is second on the Agency of Toxic Substances and Disease Registry/Environmental Protection Agency's (ATSDR/EPA) list of Top 50 Priority Pollutants, which is a ranking of toxic substances considered to be of importance at 257 National Priorities List (NPL) sites around the nation (2). The current maximum contaminant level (MCL) for drinking water supplies is 50 μg/L As (3). Arsenite is more toxic than arsenate (4). Because the properties of arsenic such as toxicity, solubility, and mobility depend on its oxidation state, determination of speciation is essential for evaluating arsenic behavior in the environment. Therefore, determination of speciation is critical for both accurate risk assessment and design of cleanup strategies.

Today the most recognized method of arsenic speciation is the hydride generation technique coupled with atomic absorption spectrophotometry (5). The method involves

sequential generation of the arsenic hydrides (arsines) of As(III) and As(V). These arsines are then swept into the atomization unit of an atomic absorption spectrophotometer where their absorbances are measured. The method provides good detection limits (< 1 ng/mL). However, a limitation of the technique is that separation of arsenic species is not performed at the time of sample collection but as the first step of the analysis. Therefore, samples need to be treated properly with a preservative at the time of collection or the concentration ratio of As(III) to As(V) may change between sample collection and analysis.

Another popular technique for the separation of As(III) and As(V) is based upon an anion-exchange scheme (6,7,8). Above pH 2 arsenate exists as a negatively-charged species ($H_2AsO_4^-$, $HAsO_4^{2-}$); whereas up to pH 9, arsenite exists as a neutral species (H_3AsO_3) (9). The sample solution is passed through a column packed with strongly basic, anion-exchange resin. Being neutral in the pH range of most natural water samples, As(III) is not retained by the resin and is collected in the first fraction. In contrast, As(V), being charged at most natural pH's, is retained and is then eluted into a later fraction with HCl. After separation, graphite furnace atomic absorption spectrophotometry (GFAAS) is used to determine the concentration of the two As species. The appeal of the anion-exchange technique is that the separation step is simple and eliminates the potential problem of sample storage by allowing for in-field separation of the As species.

The purpose of this research was to improve the anion-exchange speciation technique and to apply the refined technique in several studies involving the reduction/oxidation (redox) behavior of arsenic. Separation schemes were developed using the traditional anion-exchange resin and the recently available anion-extraction disks. In one study, the

technique was used to determine the speciation of arsenic when combined with various redox-active substances (i.e., Fe(II), O_2, MnO_2). The redox behavior of arsenic is dependent on pH and the redox potential (E_H). Second, an investigation of the redox behavior of arsenic, in a soil slurry, was conducted using a reactor system capable of controlling pH and E_H. Third, the technique was applied in the field to determine arsenic speciation in creek water at Sutter Creek, Ca., where homes are built upon a large pile of mine tailings containing arsenic. Fourth, a sample of the mine tailings was collected, placed in a reactor, and combined with a soil slurry thus simulating a flooded condition. While the pH and E_H were monitored, arsenic speciation was determined as conditions became more reducing due to microbial action.

An investigation of zinc amalgam as a reductant constitutes the second part of this thesis. Chemical reduction techniques are commonly used in situations in which a sample constituent must be converted to a particular oxidation state to effect its determination (10,11). Common reductants include zinc or silver amalgams, dithionite, Sn(II) chloride, ascorbic acid, or titanium citrate. For example, in the titrimetric determination of iron, the ferric iron is converted to the ferrous form by a reducing agent. The ferrous form and thus total iron is determined by titration with permaganate or dichromate (10). Reductants are commonly used in the study of microbiological systems in which a medium with a low redox potential is required for culture of anaerobic bacteria. A reductant is added to the culture medium to eliminate the oxygen and thus promote rapid growth of the anaerobic bacteria while preventing the growth of facultative anaerobes (12). Reductants also find use in the study of redox transformations involving specific one-on-one interactions of various environmental couples or indicators of environmental redox

conditions. For example, the reductant Fe(II) has been used in synthetic studies to reduce Cr(VI) and redox indicators (13).

Presented here is a study of the reduction capabilities of zinc amalgam as it applies to the reduction of Cr(III) and redox indicators (e.g., thionine, phenosafranine). Zinc amalgam, in the classic Jones Reductor configuration, provides a simple technique for production of Cr(II) and reduced forms of various redox indicators. Also, zinc amalgam and titanium (III) citrate are compared based on their reduction of the redox indicator thionine.

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Chapter 2
Development and Application of an Arsenic Speciation Technique Using Ion-Exchange Solid Phase Extraction Coupled with GFAAS

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2.1 Introduction and Historical

2.1.1 Environmental Overview

Arsenic ranks 20th in abundance in the earth's crust occurring mainly in igneous, sedimentary rocks, and particularly sulfidic ores. Typical crustal concentrations can range from 0.1 to several hundred μg/g (1). Table 2.1 lists the arsenic concentration in geological materials (2). Table 2.2 shows arsenic as being widely used in pigments, insecticides and herbicides, as a metal alloy, and in chemical warfare agents (3).

Arsenic is toxic and believed to be carcinogenic (4). Toxicity increases from the +5 (arsenate) to the +3 (arsenite) oxidation state with arsine and trimethylarsine gases being even more toxic (5). Arsenic toxicity is inversely related to the rate of excretion of the arsenical from the body. The increased toxicity of As(III) is due to its ability to react with sulfhydryl groups thus increasing its residence time in the body (6). The greatest health hazard exists through ingestion of arsenic-laden waters. The current maximum contaminant level (MCL) for drinking water supplies is 50 μg/L As (2). Due to increased anthropogenic activity (i.e., sulfur ore mining, fossil fuel burning, land erosion, etc.), levels of arsenic entering oceans alone have increased by a factor of 3 (1). In recent news (7), the town of Sutter Creek, Ca. has experienced outbreaks of arsenic poisoning as a result of a subdivision being built on a arsenic tailing pile. The tailing pile is a byproduct of a deep-shaft gold mining operation in the area.

Arsenic, like trace metals, is cycled in the environment. Dissolution in water mobilizes arsenic with aquatic and soil/sediment concentrations being controlled by many factors

Table 2.1 Arsenic Concentration in Geological Materials

Type of rock	*Arsenic (mg/kg)*
Igneous	
Ultrabasic	
Periodotite, dunite, serpentinite	0.3 - 15.8
Basic	
Basalt (extrusive)	0.18 - 113
Gabbro (intrusive)	0.06 - 28
Intermediate	
Latite, andesite, trachyte (extrusive)	0.5 - 5.8
Diorite, granodiorite, syenite (intrusive)	0.09 - 13.4
Acidic	
Rhyolite (extrusive)	3.2 - 5.4
Granite (intrusive)	0.18 - 15
Metamorphic rocks	
Quartzite	2.2 - 7.6
Slate/phyllite	0.5 - 143
Sedimentary rocks	
Marine	
Shale/claystone (nearshore)	4.0 - 25
Shale/claystone (offshore)	3.0 - 490
Carbonates	0.1 - 20.1
Phosphorites	0.4 - 188
Sandstone	0.6 - 9
Nonmarine	
Shales/claystone	3.0 - 12

Taken from Welch, A. H., Lico, M. S., and Hughes, J. L. Ground Water 1988, 26, 333

Table 2.2 Main Modern Uses of Arsenic Compounds

Sector	Uses
Agriculture	Pesticides, insecticides, defoliants, wood preservatives, debarking trees, soil sterilant
Livestock	Feed additives, disease prevention (swine dysentery, heartworm infection), cattle and sheep dips, algaecides
Medicine*	Antisyphilitic drugs, treatment of trypanosomiasis, amebiasis, sleeping sickness
Electronics	Solar cells, optoelectronic devices, semiconductor applications, light-emitting diodes (digital watches)
Industry	Glassware, electrophotography, catalysts, pyrotechnics, antifouling paints, dyes and soaps, ceramics, pharmaceutical substances
Metallurgy	Alloys (automotive body solder and radiators), battery plates (hardening agents)

*Arsenic still used for medicinal purposes in some developing countries.

Taken without permission from Nriagu, J. O., Arsenic in the Environment Part 1: Cycling and Characterization, John Wiley and Sons: New York, 1994.

such as oxidation/reduction, ligand exchange, precipitation, and adsorption. A more detailed discussion is presented in Appendix A. Table 2.3 lists common acid/base and oxidation/reduction reactions of arsenic.

The environmental behavior of arsenic is dependent on the actual chemical form present. Arsenic has four stable oxidation states: +5, +3, 0, and -3. States 0 and -3 rarely occur in natural systems (1). From thermodynamic data, redox potential (E_H) vs. pH diagrams can be constructed which are useful for predicting predominate forms of As in the environment. Figure 2.1 shows a typical E_H-pH diagram for a total arsenic concentration of 10 μM (1). At higher E_H values, the +5 state predominates as the arsenic acid species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}). When conditions become more reducing, lower E_H values, the +3 state dominates as the arsenious acid species (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$). The range of water soluble arsenic species is pH dependent. When sulfide is present, realgar (AsS) and orpiment (As_2S_3) occur as stable solids below pH 5.5 and an E_H of 0 V. Below pH 5.5, the predominate sulfidic aqueous species is $HAsS_2$ with a solubility of $10^{-6.5}$ mol/L, while above pH 5.5, AsS_2^- is the predominate species with a solubility of 10^{-5} mol/L (1).

At extremely low E_H values and in the presence of methylating organisms, arsines and organoarsenicals may be formed. Organoarsenical species such as monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) are known to exist as products of biomethylation (2). The toxicity of the organoarsenicals is considered less than that of the inorganic arsenicals (6). The study in this thesis focuses on the speciation of the more prevalent and toxic inorganic arsenic forms.

Table 2.3 Acid/Base and Oxidation/Reduction Reactions of As(III) and As(V)

Acid - Base Equilibria

Arsenic Acid (As(V))

$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+$	$pK_{a1} = 2.24$
$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+$	$pK_{a2} = 6.96$
$HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H^+$	$pK_{a3} = 11.50$

Arsenious Acid (As(III))

$H_3AsO_3 \rightleftharpoons H_2AsO_3^- + H^+$	$pK_{a1} = 9.29$
$H_2AsO_3^- \rightleftharpoons HAsO_3^{2-} + H^+$	$pK_{a2} = 12.10$

Reduction Half-Reactions

As(V) - As(III)	E_H° *(V)*
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O$	0.58
$H_2AsO_4^- + 3H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O$	0.64
$HAsO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O$	0.86
$HAsO_4^{2-} + 3H^+ + 2e^- \rightleftharpoons H_2AsO_3^- + H_2O$	0.58
As(III) - As(0)	
$H_3AsO_3 + 3H^+ + 3e^- \rightleftharpoons As(s) + 3H_2O$	0.23
$H_2AsO_3^- + 4H^+ + 3e^- \rightleftharpoons As(s) + 3H_2O$	0.41
As(0) - As(-III)	
$As(s) + 3H^+ + 3e^- \rightleftharpoons AsH_3 + H_2O$	-0.61

Taken without permission from Scott, M. J. Ph. D. Thesis, California Institute of Technology, 1990.

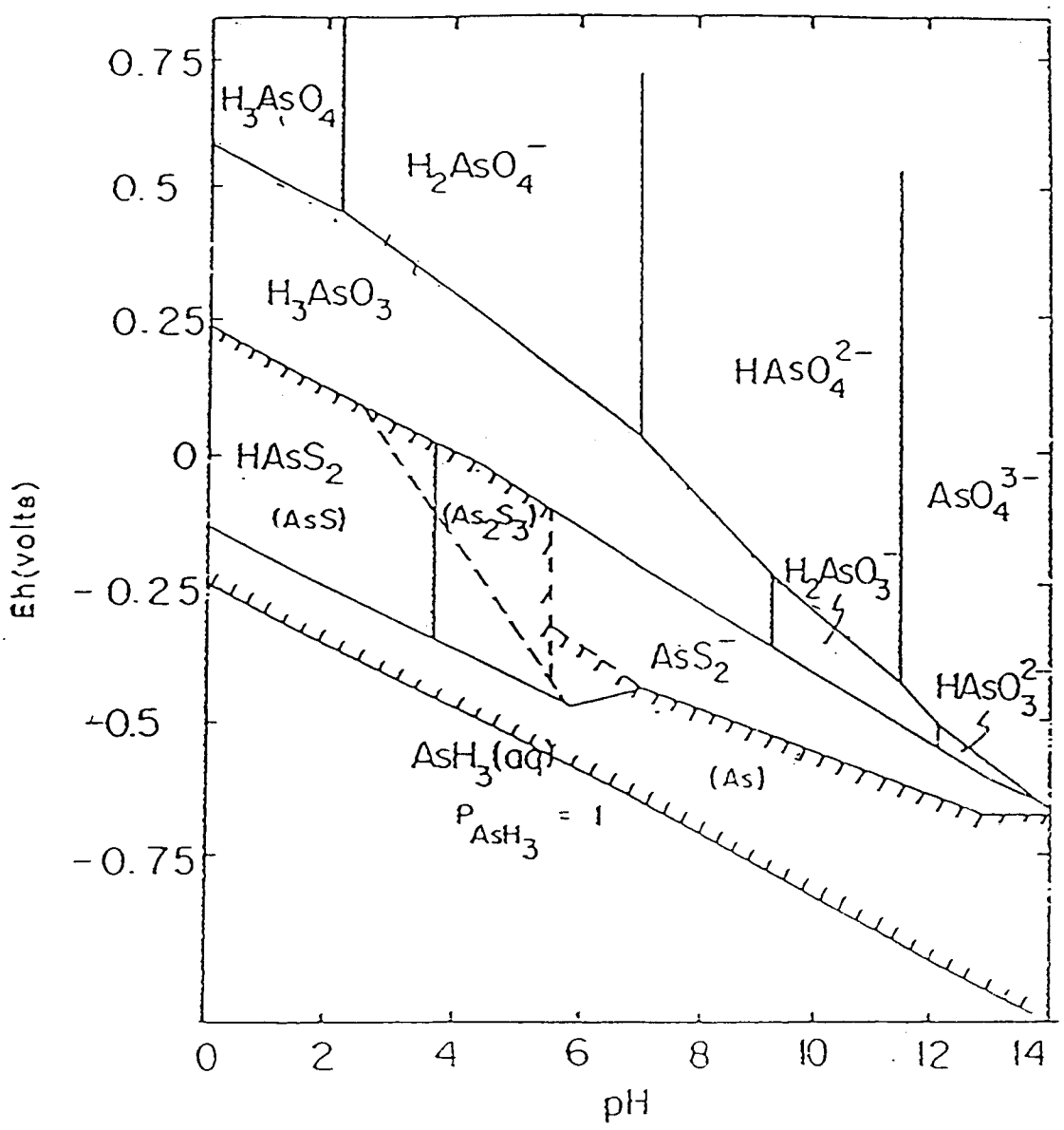

Figure 2.1 E_H - pH diagram for As at 25°C and one atmosphere. Total arsenic is 10 μM and total sulfur is 1 mM. Solid species, with solubilities low enough to occur in this system, are represented in parentheses. The cross-hatched area, which indicates solubility less than 5 μM, represents the area of occurrence for the solid species.

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2.1.2 Detection of Arsenic

Table 2.4 lists several methods for determination of arsenic along with their detection limits. The most popular technique for the determination of arsenic has been and continues to be atomic absorption spectrophotometry (AAS) (8). Recently, inductively coupled plasma emission or mass spectrometry methods have gained in popularity. In AAS, there exists different options for both sample introduction and atomization of arsenic.

Currently, the most accepted technique for the determination of arsenic is the hydride generation technique coupled with atomic absorption spectrophotometry with a quartz tube atomizer. Direct aspiration of samples into flame atomizers is not popular because detection limits are poor (typically 3000 ng/mL), high absorption by the flame of the arsenic source line at 193.7 nm causes noise problems, and interfering species may form within the flame. Detection of arsenic as an arsine following hydride generation has been accomplished through DC discharge, flame ionization, electron capture, and atomic absorption spectrophotometry (9, 20,11). For the majority of hydride generation techniques using AAS, the hydrides have been passed directly into the flame or into a heated quartz absorption cell or tube. The cell or tube is heated electrically or by a flame. Use of a quartz cell or tube results in significantly better detection limits (typically 1 ng/mL) as compared to direct aspiration into the flame without hydride generation. Detection limits are significantly lower in quartz cells because of the longer residence times and less dilution of the atomized sample by flame gases (8).

Table 2.4 Comparison of various instrumental methods for determination of arsenic

Technique	Detection Limit (ng/mL)	Ref.
Atomic Absorption Spectrophotometry (AAS)		
Flame -- air-acetylene	3000	8
- hollow cathode lamp	2300	41
- electrodless discharge lamp	150	41
argon-hydrogen	100	8
Graphite Furnace AAS	0.2 - 1	8, 26
Atomic Emission Spectrometry		
dc plasma	100	8
inductively -coupled plasma (ICP)	4	44
ICP/MS	0.002 - 0.01	5
Atomic Fluorescence Spectrometry	100	8
Neutron Activation Analysis	<1	26
X-ray Fluorescence Spectrometry	0.05	26
Colorimetry		
Silver diethyldithiocarbamate	10 - 100	26
Molybdenum Blue	~1	26
Differential Pulse Polarography	2 - 6	26
Hydride Generation		
dc discharge emission spectrometry	0.02	26
AAS		
Flame-in-tube	0.2	42
Quartz tube	0.8	43

Total arsenic has been determined by AAS with a graphite furnace atomizer. Initially, because of the volatility of arsenic, the success of the technique was in doubt. However, with nickel or palladium matrix modifiers, arsenic can be stabilized in the furnace during the ash step. Use of hydride generation coupled with the graphite furnace should provide good detection limits but because of the technical difficulty in the combined process, there are few references about the technique (8).

2.1.3 Determination of Arsenic Speciation

Hydride generation and ion-exchange are two popular techniques for the separation of arsenic species prior to detection. Other methods for the determination of arsenic speciation include colorimetric (16) and electrochemical procedures (11,18). Yu and Wai (15) used chelation of arsenite by bis(trifluoroethyl)dithiocarbamate coupled with gas chromatographic separation and electron capture detection to determine arsenite and arsenate.

At present, hydride generation of volatile arsines from the various arsenicals is the most popular technique for separation of arsenic species (8). In the last two decades, the majority of aquatic speciation studies of arsenic have employed Braman's (9) hydride generation technique or an adaptation thereof (10,11,12,13). The technique involves generation of the arsines by reduction with zinc amalgam or sodium tetraborohydride solution (8). The reduction reaction is pH dependent and the arsenicals are reduced at a pH related to their pK_a: the oxyanions of As(III) and As(V) need to be fully protonated

for reduction to the arsines. After the arsine of a given species is formed, it is swept into the atomization unit of the AA spectrophotometer.

In some analysis, total As is measured initially by adjusting the sample to pH 1-2. In a separate analysis with another aliquot of sample, the As(III) concentration is determined by buffering to pH 4-5. At this pH, only the arsine of As(III) is formed. The As(V) concentration is then taken as the difference between these two measurements. Alternatively, one aliquot of sample is used and a determination of As(III) is made at pH 4-5 after which the sample is adjusted to pH 1-2 and the As(V) concentration is measured.

The hydride method is also capable of determining the concentration of the organoarsenicals. The arsines of these compounds are formed at the same pH as that for As(V). Separation of the arsines generated from As(V) and the organoarsenicals is accomplished by trapping the arsines in a liquid nitrogen cooled U-trap. The arsines are then detected by sequentially sweeping them into the detection unit by means of a carrier gas directed through the arsine generator and U-trap. The trap is slowly heated to drive off the arsines in the order of their boiling points (arsine: -55°C, methylarsine: 2°C, dimethylarsine: 55°C). Through the virtue of differing pK_a's and boiling points, the various arsenic species are effectively separated. Packing the trap with chromatographic material (i.e., glass beads, silanized wool, Porapak Q, molecular sieves) improves the resolution of the separation (9,10,11). Various other traps have also been employed to eliminate possible interferences from water, hydrogen sulfide, or carbon dioxide.

Ion-exchange coupled with atomic spectrophotometry is another novel separation/detection scheme. Arsenic species are separated as a result of possessing different charges, based upon their pK_a, at a given pH. For example, at pH values greater

than 2, soluble As(V) is present as a negatively-charged species ($H_2AsO_4^-$, $HAsO_4^{2-}$) while soluble As(III) exists as a neutral species (H_3AsO_3) up to pH 9. Separation is achieved through the use of an anion-exchange resin. Being neutral, As(III) will not be retained by the resin, while As(V), being charged, will be retained. The As(V) is eluted from the resin by passing HCl, trichloroacetic acid, or another eluent through the resin.

Grabinski (38) used a mixture of cation and anion-exchange resins to separate arsenite, arsenate, MMAA, and DMAA. The elution scheme was as follows: with 0.006 M trichloroacetic acid (pH 2.5), arsenite and then MMAA were eluted; 0.2 M trichloroacetic acid eluted arsenate; 1.5 M NH_4OH followed by 0.2 M trichloroacetic acid eluted DMAA. The arsenic in each fraction was detected with electrothermal atomic absorption spectrophotometry.

Ricci et. al. (12) used a Dionex anion column (3 x 500 mm) to separate effectively arsenite, arsenate, MMAA, DMAA, and p-aminophenyl arsenate using a mixture of 0.0024 M $NaHCO_3$/0.0019 M Na_2CO_3/0.001 M $Na_2B_4O_7$ as eluent. All the compounds are separated except As(III) and DMAA which must be separated with a lower ionic strength eluent in a separate analysis. The detection system utilized continuous arsine generation followed by quartz furnace atomization and atomic absorption spectrophotometry.

Henry and Thorpe (19) used separate cation- and anion-exchange columns to achieve separation of As(III), MMAA, and DMAA, followed by determination of total As after which As(V) was determined by difference. The sample was divided into four aliquots. The first two aliquots were used for determination of As(III) and total inorganic arsenic by means of a differential pulse polagraphy method developed by the authors. The As(V)

concentration was taken as the difference between these two measurements. The third aliquot was passed through a cation-exchange resin which isolated the DMAA. The DMAA was then eluted with 1 M NaOH. The fourth aliquot was passed through an anion-exchange resin which isolated the MMAA and the As(V). The MMAA and As(V) were then sequentially eluted from the resin with an eluent containing a total acetate concentration of 0.1 M. Determination of DMAA and MMAA were accomplished by reduction to As(III) with SO_2 followed by determination of the As(III) by differential pulse polarography.

Ficklin (14) developed one of the simplest ion-exchange methods for separation of arsenite and arsenate. The As(III) and As(V) were separated on a 10 cm x 7 mm column packed with Dowex 1x8, 100-200 mesh, strong anion-exchange resin in the acetate form. The resin was converted to the acetate form by passage of 1 M NaOH followed by 1 M acetic acid through the resin. Samples were acidified to 0.12 M with concentrated HCl and passed through the column. Reportedly, the As(V) was retained by the resin in the acetate form whereas the As(III) was not. The As(V) was then eluted by passage of 15 mL of 0.12 M HCl through the column. With a 5-mL sample size, four 5-mL portions were collected. Arsenite is eluted in the first two fractions and arsenate is eluted in the last two. The concentration of arsenic in each portion was then determined by graphite furnace atomic absorption spectrophotometry with Ni matrix modification. The method was used for in-field separation of arsenic species (39).

Presented here is a refined anion-exchange technique for the speciation of arsenic. Separation schemes were developed using the traditional anion-exchange resin and the recently available anion-extraction disks. The refined technique was applied in the study

of the redox behavior of arsenic. First, the technique was used to determine the speciation of arsenic when combined with various redox-active substances (i.e., Fe(II), O_2, MnO_2). Second, an investigation of the redox behavior of arsenic, in a soil slurry, was conducted with a reactor system capable of controlling pH and E_H. Third, the technique was applied in the field to determine arsenic speciation in creek water at Sutter Creek, Ca., where homes are built upon a large pile of mine tailings containing arsenic. Fourth and finally, a sample of the mine tailings was collected, placed in a reactor, and combined with a soil slurry thus simulating a flooded condition. Both the pH and E_H were continually monitored and arsenic speciation was determined as conditions became more reducing due to microbial action.

2.2 Experimental

All solutions were prepared with DI H_2O obtained from a Millipore Milli-Q system. All reagents were reagent grade and were weighed with either a Sartorious Type 1106 top-loading balance (± 0.01g) or a Mettler Type H15 analytical balance (± 0.2 mg). All As(III) and As(V) standard solutions were prepared from 1000 mg/L stock solutions prepared as follows:

As(III) dissolve 1.3204 g of As_2O_3 (Mallinckrodt) in 500 mL of 0.05 M NaOH, neutralize with HCl, and dilute to 1000 mL with DI H_2O.

As(V) dissolve 1.6028 g of As_2O_5 (Alpha Products) in 1000 mL of DI H_2O.

Arsenic standards were prepared in clean Pyrex glass volumetric flasks and allowed to stand in the designated flask for 24 hours. The solutions were then discarded, the flasks were copiously rinsed with DI H_2O, and the standard solutions were remade in the same flasks. Solution delivery and dilutions were made with an EDP-2 Eppendorf pipette. All pH measurements were performed with a pH glass electrode (Analytical Sensors, Inc., PH10107B-03-B) and an analog pH meter (Jenco Model 603A).

2.2.1 Instrumentation

Arsenic concentrations were initially determined with a Varian Techtron AA-6 atomic absorption (AA) spectrophotometer with a CRA Model 90 graphite furnace assembly along with an arsenic hollow cathode source (CPI). A wavelength of 193.7 nm was used for all measurements. Sample volumes of 10 µL were injected manually with an

Eppendorf pipette. Peak heights were recorded with a Linear Instruments Model 555 chart recorder. Nitrogen gas was used to provide an inert atmosphere around the graphite furnace. Background correction was not used. The majority of the Varian work was aimed at resolving the elution position of the arsenic species.

Eventually, all concentration measurements were performed with a Perkin Elmer Zeeman/3030 AA spectrophotometer with a HGA 600 furnace assembly. The instrument is equipped with Zeeman background correction. Sample volumes of 20 μL were automatically injected into a L'vov platform graphite furnace with a Perkin Elmer AS-60 autosampler. Data were recorded with a Perkin Elmer PR-100 printer. An As EDL (Perkin Elmer) operated at 13 W was used as a source. The temperature program used for each instrument is listed in Table 2.5. The Zeeman/3030 spectrophotometer offers computer control thus making data collection and analysis relatively simple. Both peak area and peak height were reported by the instrument but the integrated peak area was used in the calculation of arsenic concentration. Another feature of the instrument is the gas stop utility which enables the user to shut off the argon purge gas during the atomization step. The arsenic atoms will not be swept out of the furnace but will remain in the light path which results in increased signals. A detection limit of 2 μg/L was obtained with this instrument.

Nickel matrix modification was used for all arsenic concentration measurements. Nickel stablizes the arsenic in the furnace by forming a less volatile nickel arsenide which prevents significant loss of the normally volatile arsenic during the drying and ashing stages (5). For experiments performed on the Varian spectrophotometer, 80 μL of a 1000 mg/L Ni solution, made by dissolving 2.5 g $Ni(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt) in

Table 2.5 Instrumental Operating Parameters for Varian and Perkin Elmer Graphite Furnace Atomic Absorption Spectrophotometers

Varian AA6 [a]

Step	*Time (s)*	*Temp (°C)*
Dry	40	100
Ash	15	900
Atomize (ramp 300°C/s)	3	2100

Perkin Elmer Zeeman/3030 [b]

Step	*Time (s)*	*Temp (°C)*
Dry	60	120
Ash	25	1300
Atomize (ramp max.)	4	2300
Clean	6	2600
Cool	4	20

[a] Conditions optimized for maximum peak height with a 100 µg/L As(III) standard solution.

[b] Conditions recommended by manufacturer except the dry step.

500 mL of DI H_2O, were added to 1 mL of sample or standard, in sample cup, prior to injection into furnace. For experiments with the Perkin Elmer spectrophotometer, 100 µL of a 833 mg/L solution, made by dissolving 2.1 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 500 mL of DI H_2O, were added to 900 µL of sample or standard, in the sample cup, prior to injection into the furnace.

The optimization of the concentration of Ni to use in experiments with the Varian spectrophotometer was performed with a 500 mg/L Ni solution and a 0.4 mg/L As(III) solution. Five solutions were prepared in either a 25-mL or 50-mL volumetric flask according to the following scheme:

Final Ni concentration (mg/L):	10	40	100	200	400
Volume As(III) (µL)	20	10	10	10	10
Volume Ni(II) (mL)	1	2	5	10	20
Total Volume (mL)	50	25	25	25	25

Nickel optimization for the Perkin Elmer spectrophotometer was performed with a 833 mg/L Ni solution and a 50 µg/L As(III) solution. Solutions with a total volume of 1 mL were prepared directly in the sample cup by injecting 900 µL of the 50 µg/L As(III) solution into the cup. Various volumes of the Ni solution and DI H_2O were then injected into the cup according to the following scheme:

Final Ni concentration (mg/L):	0	17	33	50	67	83	167
Volume Ni(II) (µL)	0	20	40	60	80	100	100
Volume DI H_2O (µL)	100	80	60	40	20	0	0

The 167 mg/L Ni solution was prepared with 100 µL of a 1666 mg/L Ni stock solution.

Separate calibration curves had to be constructed for As(III) and As(V). Calibration standards of 0.03, 0.1, 0.2, and 0.5 mg/L were used for the Varian spectrophotometer, while standards of 0.02, 0.05, and 0.1 mg/L were used for the Perkin Elmer spectrophotometer. The As(III) standards were prepared in DI H_2O, while As(V) standards were prepared in 0.1 M HCl.

2.2.2 Initial Separation Studies

2.2.2.1 Resin Technique

Dowex 1x8 anion-exchange resin (100-200 mesh), in the chloride form, was obtained from Aldrich. Properties of the resin are listed in Table 2.6 (50). A list of counterion selectivites, defined as the affinity of various anions for the resin, is given in Table 2.7. Duplication of Ficklin's method (14) was attempted initially. About 2 - 3 g of the resin was slurry packed into a glass Bio-Rad Econo-column (10 cm x 7 mm). The procedure for conversion of the resin to the acetate form and separation of arsenic species, as recommended by Ficklin, is listed in Table 2.8.

The initial column setup is illustrated in Figure 2.2. Approximately 5 mL of 0.5 mg/L As(III) or As(V) were pipetted on to the column. Arsenite is not retained by the acetate form of the resin and therefore elutes first. Arsenate was eluted by passage of 15 mL of 0.12 M HCl. Gravity flow was recommended (14) but proved time consuming. Therefore, pumping (Pharmicia Peristaltic Pump P-3) at a flow rate of 3-4 mL/min was used instead. Fractions were collected in 1-mL aliquots in order to resolve the elution position of As(III) and As(V). The twenty 1-mL fractions were then analyzed by GFAAS.

Table 2.6 Properties of Anion-Exchange Resin and Extraction Disk

Property	Resin[a]	Extraction Disk[b]
Active group	quaternary amine	quaternary amine
Resin base	styrene divinylbenzene copolymer	styrene divinylbenzene copolymer--Teflon
Capacity	1.2 meq/mL	0.043 meq (useful)[c]
Ionic form	chloride	chloride
Mesh/pore size	100-200 mesh (74 - 149 μm)	80 Å

[a] Dowex 1x8 strong anion-exchange resin
[b] Empore Extraction Disk with Anion-Exchange SR
[c] This value is calculated by multiplying the normal capacity of the 47-mm disk (0.56 meq (useful)) by $(13/47)^2$. This normalizes the capacity to that of a 13-mm disk.

Table 2.7 Relative Selectivity of Various Anions for the Resin.

Counterion	*Relative Selectivity for Resin*[a]
I^-	175
ClO_3^-	74
NO_3^-	65
Br^-	50
CN^-	28
Cl^-	22
HCO_3^-	6
HPO_4^-	5
Acetate	3.2
F^-	1.6
OH^-	1.0

[a] The scale is relative to hydroxide anion

Taken without permission from: AG 1 and AG 2 Strong Anion Exchange Resin Instruction Manual, Bio-Rad Laboratories, Hercules, Ca.

Table 2.8 Conditioning and Separation Protocols used with Resin and Disks

Ficklin's Method

Conditioning	*Separation*
- 3 mL of 1 M NaOH	- 5 mL of sample or standard
- 15 mL of DI H_2O	- 15 mL of 0.12 M HCl
- 5 mL of 1 M HAc	
- 5 mL of DI H_2O	

Modified Method [a]

Conditioning	*Separation*
- 5 mL of 1 M HCl	- 5 mL of sample or standard
- 20 mL of 1 M NH_4OH	- 5 mL of 0.1 M HAc
- 10 mL of 1 M HAc	- 10 mL of 0.1 M HCl
- 5 mL of DI H_2O	

Initial Disk Method [a]

Conditioning:	*Separation:*
- 10 mL of 1 M HCl	- 3 mL of sample or standard
- 5 mL of 1 M NH_4OH	- 3 mL of 0.05 M HAc
- 5 mL of 1 M HAc	- 3 mL of 0.1 M HCl
- 5 mL of DI H_2O	

[a] A cleaning procedure with two alternate washes of 10 mL of 1 M HCl and 10 mL of 1 M NH_4OH, ending with NH_4OH, was used prior to final conditioning described above.

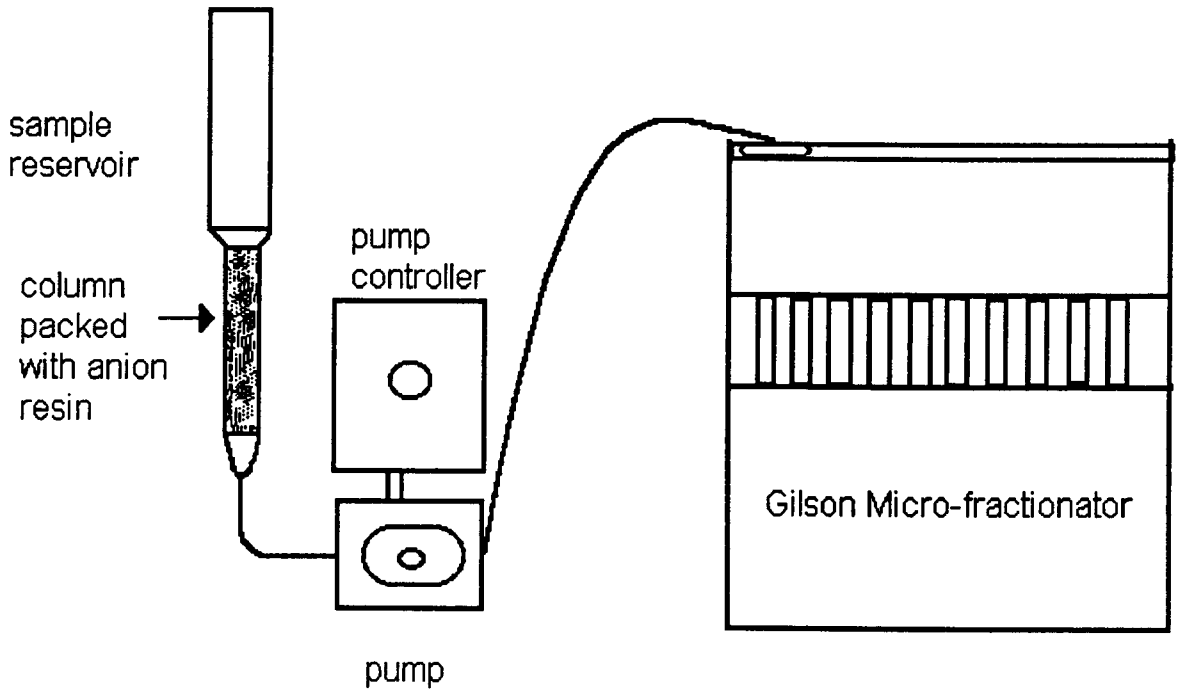


Figure 2.2 Schematic of Initial Column Setup

Several adjustments to Ficklin's original method were made. The modified protocol for conditioning and elution of arsenic species is listed in Table 2.8. First, a smaller Bio-Rad column, 5 cm x 5 mm, was used with about 1 g of resin. The smaller bed volume reduced conditioning and elution times and conserved resin. Second, the resin was extensively cleaned, prior to final conditioning, with alternate 10-mL washes of 1 M HCl and 1 M NH_4OH. Third, larger volumes of the conditioning solutions were used to improve the retention of As(V). Increasing the volume of conditioning solutions and decreasing the amount of resin resulted in more complete conversion of the resin to the acetate form. The DI H_2O rinse between the NaOH (NH_4OH) and HAc rinses was eliminated because it did not affect the resolution of the two As species. Fourth, a solution of 1 M NH_4OH was used to condition the resin instead of NaOH because of the molecular absorption by sodium salts during the AA determination of arsenic. Fifth, an elution step with acetic acid (HAc) was added to remove the As(III) remaining in the resin bed prior to elution with HCl. This step provided a cleaner separation between As(III) and As(V) and also eliminated HCl, which suppressed the As(III) signal, from the second As(III) fraction. The volumes and concentrations of conditioning and eluting solutions were varied and optimized in several experiments until a "clean" separation of As(III) and As(V) in DI H_2O was obtained with minimal volumes of eluent solutions.

The suppression of the As(III) AA signal, but not the As(V) signal, by HCl was subsequently used as a qualitative test for the presence of As(III). Testing for the presence of As(III) was performed by injecting 10 μL of concentrated HCl into 1 mL of sample in the GFAAS sample cup prior to analysis.

After the elution patterns of As(III) and As(V) were established, four 5-mL fractions, instead of 20 1-mL fractions, were collected in Corning Pyrex culture tubes with a Gilson Micro-Fractionator. The As(III) elutes in fractions 1 and 2, while the As(V) elutes in fractions 3 and 4. Even though As(III) is not retained by the acetate form of the resin, it is not completely eluted into the first fraction because of hold-up in the interstitial volume of the resin.

At this point, the remainder of arsenic concentration measurements were performed with the Perkin Elmer spectrophotometer. The first pump was replaced with another pump, capable of higher flow rates (FMI Lab Pump RHV with a Stroke Rate Controller, Model VT100), which decreased the time required for column conditioning. This setup was not the most efficient and eventually the column method was developed to where 1 g of resin was packed into Bio-Rad Polypropylene Econo-columns (4 in x 0.25 in) and these columns were then used in conjunction with a vacuum manifold (J.T. Baker). The setup is schematically shown in Figure 2.3. The final protocol for conditioning and elution is listed in Table 2.9. It differs from the modified protocol primarily in the use of DI H_2O for elution of As(III) in the second fraction.

2.2.2.2 Extraction Disk Technique

Empore™ extraction disks with anion-exchange SR (J.T. Baker) were also used for separation of arsenic species. The disks consist of a matrix of PTFE (polytetrafluoroethylene) impregnated with strong anion-exchange resin. Properties of the disks are listed in Table 2.6 (51). The selectivities of anions for the disk are similar to

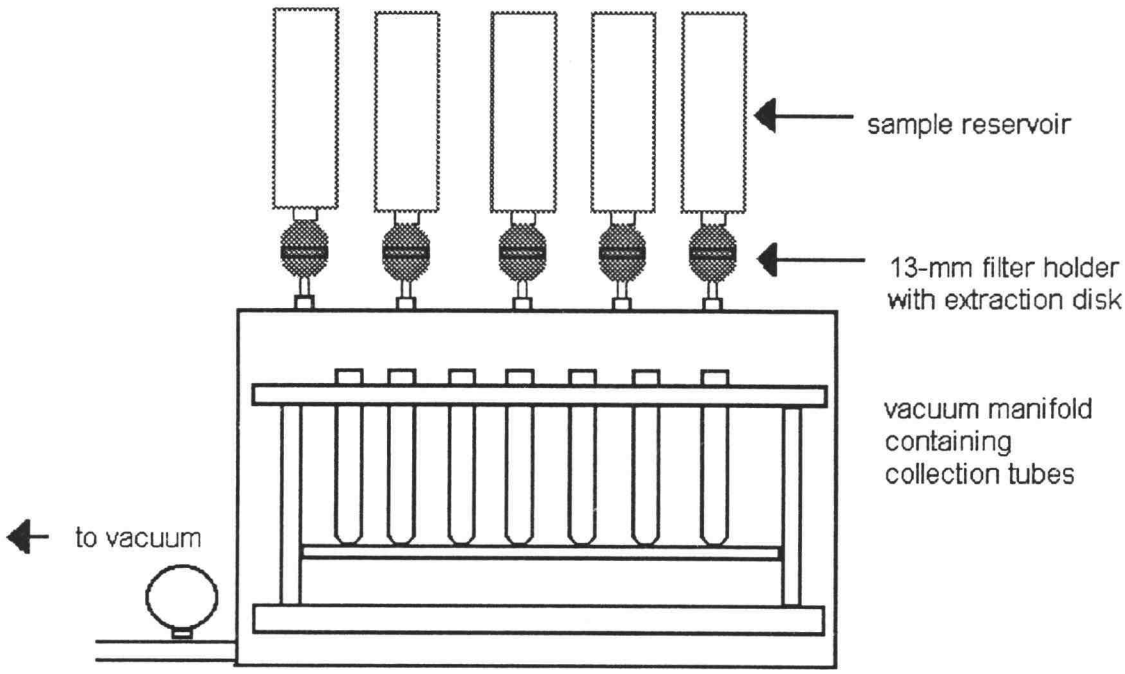


Figure 2.3 Schematic of Disk Setup. The setup is similar to the one eventually used in the resin technique.

Table 2.9 Final Conditioning and Separation Protocols for either Extraction Disks or Anion Resin.

Conditioning Procedure:

Disk	*Resin*
- alternate washes of 1 M HCl and 1 M NH_4OH [a]	- same as Disk
- 10 mL of 1 M HCl	
- 5 mL of 1 M NH_4OH	
- 5 mL of 1 M HAc	

Elution Procedure:

Disk	*Resin*
- 2-5 mL of sample	- 2-5 mL of sample
- 2-5 mL of DI H_2O	- 2-5 mL of DI H_2O
- 5 mL of 0.1 M HCl	- 10 mL 0.1 M HCl

[a] This is a cleaning step which involves 2 alternate washes with 1 M HCl and 1 M NH_4OH, ending with 1 M NH_4OH. The conditioning procedure then follows as indicated above.

those for the resin which are listed in Table 2.7. Disks with 13-mm diameters were punched out of the 47-mm disks with a cork bore and then placed in a 13-mm Swinney plastic filter holders (Gelman Science, Inc.). Plastic syringes (10-mL B-D) were used for sample reservoirs. The vacuum manifold (J.T. Baker) was used in conjunction with the extraction disks. The simple setup is illustrated in Figure 2.3. The initial protocol for conditioning and elution of arsenic species is listed in Table 2.8. The major difference between the initial disk method and the modified resin method was that smaller volumes of conditioning and eluting solutions could be used in the disk method. In particular, half the volume of 0.1 M HCl is required to elute arsenate compared to that needed for the resin. The elution patterns of As(III) and As(V) were resolved by manually collecting nine 1-mL fractions. For routine analysis, three 2- to 5-mL fractions were collected in Corning Pyrex tubes and analyzed by GFAAS.

The pH of samples and standards had to be adjusted to pH 7-8 with 0.2 M NH_4OH in order to prevent the breakthrough of As(V). At this pH, As(V) is present both as the monovalent and divalent anionic species. The divalent species, is expected, according to ion-exchange principles, to display a greater affinity for the disk thus promoting retention. In addition to the pH adjustment, breakthrough of As(V) was curtailed by use of DI H_2O as the eluent for the second fraction.

Eventually, both the extraction disk method and the column method employing the vacuum manifold could be used to achieve efficient separation of As(III) and As(V). The final protocols for conditioning and elution of arsenic species with either technique appear in Table 2.9. The conditioning protocol for both techniques is the same. With either technique, up to four samples could be processed simultaneously in about 10 min.

With the vacuum manifold, conditioning flow rates of roughly 15 - 20 mL/min were used. The elution flow rate used was regulated to roughly 5 - 10 mL/min by adjusting the vacuum intake valve.

The volume of each fraction collected was equal to the volume of sample placed on the disk or resin. In the disk method, three fractions are collected with As(III) eluting in the first two and As(V) eluting in the last. Addition of the arsenic concentrations in the first two fractions gives total As(III). Total As(V) is equal to the concentration measured in the last fraction. Four fractions are collected in the column method with As(III) eluting in the first two and As(V) eluting in the last two. Total As(III) is determined in the same manner as for the disk method; however, total As(V) is now equal to the sum of the concentrations in the last two fractions.

After conditioning and elution schemes for both techniques were finalized, five runs of either a 100 μg/L standard of As(III), 100 μg/L standard of As(V), or a mixture of 100 μg/L As(III) and 100 μg/L As(V) were performed. From these experiments, percent recoveries with standard deviations for the two separate techniques were calculated.

An additional recovery study was performed with the disk technique to evaluate the linearity over the As concentration range 0 - 100 μg/L. Seven different solutions were made with the following concentrations:

Solution No.	*As(III) (μg/L)*	*As(V) (μg/L)*
1	100	0
2	80	20
3	60	40
4	50	50
5	40	60
6	20	80
7	0	100

Duplicate separations were performed on each solution. The concentration of arsenic in each fraction was then determined with the Perkin Elmer spectrophotometer.

2.2.3 Experiments with Extraction Disks

For the experiments described below, the final protocol for conditioning and elution (Table 2.9) was used. All separations were performed in duplicate. Initially, the disk technique was used to measure the extent of oxidation of a 100 μg/L As(III) standard in its designated 100-mL volumetric flask. The oxidation in the volumetric flask and the oxidation in 7.4-mL borosilicate sample vials (Fisher Scientific) were measured and compared by transferring about 7-8 mL of the solution in flask to each of four vials labeled 0, 24, 48, and 72 hr. At the indicated times, the concentrations of the two arsenic species in the flask and the appropriate vial were determined.

The effect of competing anions Cl^- and NO_3^- on the retention of As(V) by the disk was investigated next. A stock of 100 μg/L As(V) was prepared in its designated flask. Exactly 7 mL of this solution was then placed in each of five 7.4-mL sample vials. Solutions were made to be 0, 2, 5, 10, and 20 mM Cl^- or NO_3^- by spiking with 0, 14, 35, 70, or 140 μL of a 1 M solution of $CaCl_2$ or a 1 M solution or $Ca(NO_3)_2$. The pH of the solutions was then adjusted to 7 with 1 M HAc or 1 M NH_4OH.

To evaluate preconcentration of As(V) in standards or samples with arsenic levels near or below the detection limit of 2 μg/L, standards of 1 μg/L and 10 μg/L As(V) were prepared in 100-mL volumetric flasks and allowed to sit for 24 hours. The solutions were then discarded, rinsed once with DI H_2O, and fresh solutions were made. Sample volumes

of either 2 or 20 mL were then placed on the disk and eluted. First fractions were not collected in either case, but allowed to go to waste.

As a result of the competing anion effect on the retention of As(V) by the disks, the resin technique was used for further arsenic speciation experiments where the ionic strength of solution was expected to be high. Also, with the resin technique developed, samples could be acidified to 0.01 M HCl without significant breakthrough of the As(V) into the first two fractions. However, at a level of 0.1 M HCl, breakthrough of As(V) became a problem. Approximately 1 g of the resin has more than twenty-five times the capacity of the 13-mm disk (1.2 meq vs. 0.043 meq); thus, it is able to accommodate the level of competing anions typically found in natural water samples. However, the disks were used successfully for separation of arsenic species in creek water at Sutter Creek, Ca.

2.2.4 Laboratory Studies of Redox Transformations

Laboratory redox experiments involved combining As(III) or As(V) with redox-active substances. Experiments were conducted in borosilicate sample vials with 8 mL of a 100 µg/L As(III) or As(V) standard solution. The pH values of samples were adjusted to the desired values with 1 M HAc or 0.2 M NH_4OH. Duplicate separations with 2-mL sample volumes and the final resin protocol (Table 2.9) were performed at time 0 and 24 hr. Sample vials were continually shaken between the 0- and 24-hour analysis on a rotating shaker (Labquake Shaker, LabIndustries Inc.).

2.2.4.1 Oxidation of As(III)

To test the oxidation of As(III) by hydrogen peroxide, 8 mL of 100 μg/L As(III) solution were placed in the sample vial and 50 μL of 0.1 M H_2O_2, prepared by adding 1 mL of a stock solution of 30% H_2O_2 (Mallinckrodt) to 100 mL of DI H_2O, were then injected into the vial. The pH of the solution was between 5 and 6. The "time 0" separation was performed and the vial was recapped and the solution was purged for 3-5 min with N_2.

Oxidation of As(III) by oxygen was tested next. About 25-30 mL of 100 μg/L As(III) were placed in a 40-mL borosilicate sample vial (I-Chem Research). The experiment was performed both at pH 7 and pH 8-8.5. A "time 0" separation was performed and the vial was capped and air pulled through the solution with the house vacuum.

Manganese oxides are suspected of being a significant oxidant of As(III) in the environment (21). Experiments investigating the oxidation involved combining As(III) with synthetic δ-MnO_2 (birnessite), prepared by Lemmon (24) according to the procedure of McKenzie (22). Approximately 1 g of birnessite was placed in a 40-mL sample vial (I-Chem) followed by addition of 20 mL of 100 μg/L As(III). The vial was shaken and then 6 mL of solution were removed and filtered through a 0.65-μm filter (polyvinylidene fluoride, Millipore DVPP-047-00). Two 2-mL aliquots were then taken and used for a duplicate separation at "time 0". About 1 mL of the 6-mL portion was saved and used for a total As measurement prior to separation. The vial was then purged 8 - 10 min with N_2 and placed on the rotating shaker. At 24 hours, 6 mL was removed and the procedure was repeated.

2.2.4.2 Reduction of As(V)

To investigate the reduction of As(V) by the reducing agent titanium citrate, 8 mL of 100 µg/L As(V) in 0.01 M HCl were placed in the sample vial. For a detailed discussion of how the titanium citrate was prepared, see part II section 3.2.3. The experiment was performed in HCl in an attempt to keep the oxidation product Ti (IV) from precipitating out as the hydroxide. The solution was purged with N_2 for 3 - 5 min. Next, 3 µL of 250 mM titanium citrate were injected into the vial with a Hamilton 10-µL gastight syringe. A "time 0" separation was performed and the vial was capped and purged for another 5 min.

Arsenate was next combined with ascorbic acid to investigate the apparent reduction of As(V) in natural water samples by ascorbic acid, which has been recommended (26) as a preservative for arsenic in natural water samples. Exactly 8 mL of 100 µg/L As(V) were placed in sample vial and followed by injection of 80 µL of a 1% solution of ascorbic acid, prepared by dissolving 0.5 g of L-ascorbic acid (Mallinckrodt) in 50 mL of DI H_2O. The pH was adjusted to between 6.5 - 7.

Reduction experiments combining As(V) with Fe(II) were performed at both pH 4 - 4.5 and pH 6.5 - 7. Exactly 8 mL of 100 µg/L As(V) were placed in the sample vial and the pH adjusted. The solution was then purged 3-5 min after which 20 µL of 0.05 M $Fe(ClO_4)_2$ in 0.01 M HCl were injected into the vial. Two 2-mL sample aliquots were then removed for separation and the vial was recapped and purged another 3 - 5 min.

2.2.4.3 As(V) Reduction with Multiple Components

Reduction of As(V) in the presence of various combinations of Fe(II), Fe(III), and ascorbic acid was investigated. The designation in parenthesis for each sample indicates the sequential procedure used to prepare the sample.

For the first combination sample (As(V)/Fe(II)/aerate/ascorbic acid), 8 mL of 100 μg/L As(V) were placed in sample vial followed by injection of 20 μL of 0.05 M $Fe(ClO_4)_2$ in 0.01 M HCl. The solution was then aerated by pulling air through the solution for 15 min with the house vacuum. Aeration of the sample was followed by injection of 80 μL of 1% ascorbic acid. The pH was then adjusted to 6.5 - 7.

The second combination sample (As(V)/ascorbic acid/deaerate/Fe(II)) was prepared by placing 8 mL of 100 μg/L As(V) in a sample vial followed by injection of 80 μL of 1% ascorbic acid. The pH of solution was then adjusted to 6.5 - 7 and the solution was purged with N_2 for 3 - 5 min. Finally, 20 μL of 0.05 M $Fe(ClO_4)_2$ in 0.01 M HCl were injected into the vial. Here and elsewhere, the injection of the Fe(II) solution into the vial had little effect on the pH.

To prepare the third combination sample (As(V)/deaerate/Fe(II)/ascorbic acid/deaerate), 8 mL of 100 μg/L As(V) were pipetted into a sample vial followed by adjustment to pH 6.5 - 7. The solution was then deaerated for 3-5 min. Next, 20 μL of 0.05 M $Fe(ClO_4)_2$ in 0.01 M HCl were injected into the vial followed by injection of 80 uL of 1% ascorbic acid which had been neutralized to pH 7 with 0.2 M NH_4OH. The solution was then deaerated once more.

For the fourth combination sample (As(V)/deaerate/ascorbic acid/Fe(II)/deaerate), 8 mL of 100 μg/L As(V) were placed in sample vial followed by pH adjustment to 6.5 - 7. The solution was deaerated for 3 - 5 min and followed by injection of 80 μL of 1% ascorbic acid which had been neutralized with 0.2 M NH_4OH. Next, 20 μL of 0.05 M $Fe(ClO_4)_2$ in 0.01 M HCl were injected followed by deaeration for another 3-5 min.

To prepare the fifth combination sample (As(V)/Fe(III)/ascorbic acid), 8 mL of 100 μg/L As(V) were placed in vial followed by injection of 20 μL of 0.05 M $Fe(NO_3)_3$ in 0.01 M HCl. Next, 80 μL of 1% ascorbic acid were injected into the vial. The pH was then adjusted to 7.

Finally, the sixth combination sample (As(V)/thionine/Fe(II)) was prepared by placing 8 mL of 100 μg/L As(V) in sample vial followed by injection of 40 μL of 2 mM thionine. Next, the solution was deaerated for 3 - 5 min followed by injection of 20 μL of 0.05 M $Fe(ClO_4)_2$ in 0.01 M HCl.

2.2.5 Mini-Reactor Study

A glass bioreactor (Kontes Cytostir Model 882911-0100) with two sidearms was adapted to accommodate a glass pH combination electrode (Analytical Sensors, Inc., PH10107B-03-B) and a combination Pt electrode (Analytical Sensors Inc., ORP Electrode Model OR1000031-03-B). A schematic of the apparatus is shown in Figure 2.4. A septum cap (1.7 cm x 20 mm id (Kimble) with an 18 mm x 10/90 mil septum (Alltech)) was adapted for use on one sidearm to accommodate a N_2 purge line connected to a syringe needle. A Teflon fitting was fabricated by Ted Hinke at the OSU machine shop

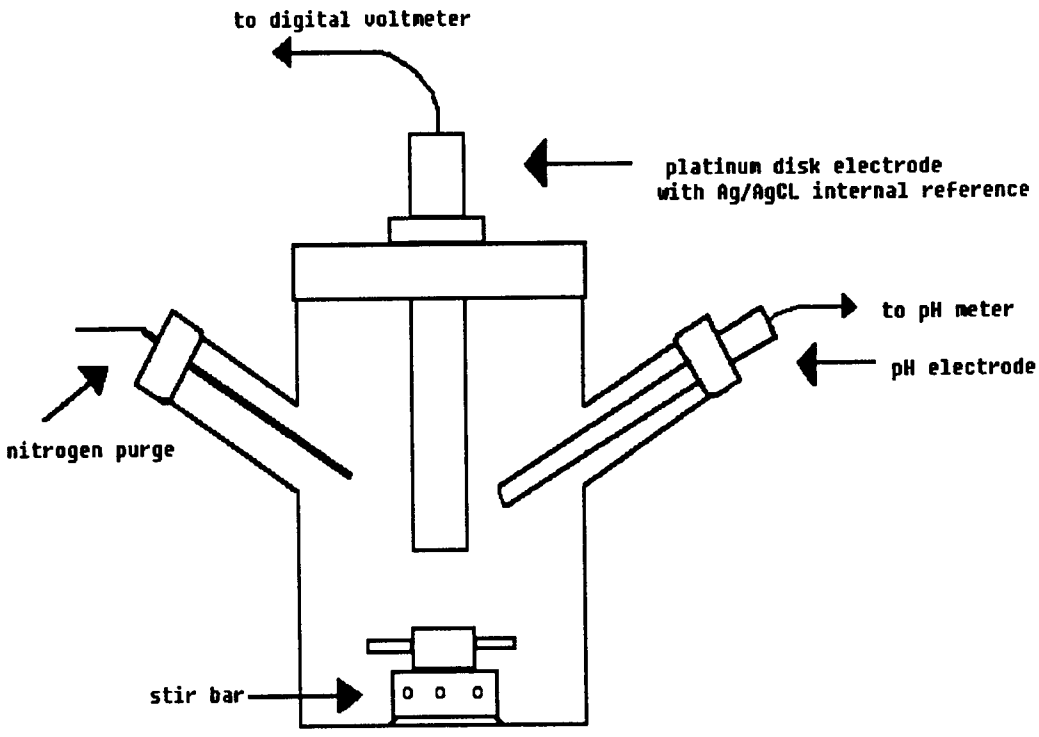


Figure 2.4 Diagram of Kontes Mini-Reactor.

and inserted into the other sidearm. This fitting was bored out to an internal diameter (~0.7 cm) which allowed the insertion of the pH electrode into the reactor. A compression cap was screwed on to the fitting to maintain a relatively airtight seal around the pH electrode while in the reactor. As purchased, the screw-on lid of the reactor has a Teflon fitting with a compression cap which accommodates a stirring shaft with a stir bar attachment at the end which extends to the top of the dome at the base of the reactor. The internal diameter of the Teflon fitting (Kontes Part No. 882916-0100) through which the stir shaft was inserted was too narrow to accommodate the Pt electrode. Therefore, a similar Teflon fitting (Kontes Part No. 882916-1000) was obtained and bored out to the proper diameter (~1.3 cm) to accommodate the Pt electrode. A compression cap was used to maintain a seal around the Pt electrode. The original stirring assembly was not used. Instead, a new Teflon stirbar assembly was fabricated to fit over the small dome in the base of the reactor. This stirbar was rotated with a stir motor (Mag-mix, Precision Scientific) to stir the contents of the reactor.

The reactor was constantly purged with N_2 during the course of the experiment. Readings of the potential at the Pt electrode versus the internal Ag/AgCl reference electrode were taken with a digital multimeter (Fluke 8020A) and were adjusted to the standard hydrogen electrode (SHE) scale by addition of 0.197 V to the measured value. Potential measurements are therefore normalized to and are reported versus SHE. The pH readings were made with the pH electrode and an analog meter (Jenco Model 603A).

After the reactor was setup, 15 g of a Bashaw A1 soil were added to the reactor. The soil was obtained from the Jackson Frazer Wetland north of Corvallis, Ore., and has been characterized by the National Resource Conservation Service (22). The soil has a clay

content of 52% (w/w) and an organic carbon content of 12.5% (w/w). Dithionite-citrate extractable Fe, As, and Mn from the <2-mm fraction were 1.7, 0.1, 0.2% (w/w), respectively. It is described as a dark, grayish brown mucky silt loam with few fine prominent strong brown mottles. It has a weak and very fine granular structure and is very friable, nonsticky, and nonplastic. There are many very fine and fine roots present.

The soil was placed in the reactor along with 300 mL of DI H_2O, 0.22 g of $CaCl_2 \cdot 2H_2O$ (Baker), and 0.02 g of NH_4Cl (EM Science) to yield concentrations of 5 mM $CaCl_2$ and 1 mM NH_4Cl. The reactor was then capped, the Pt electrode inserted, and the N_2 purge was started. After 5 days, E_{Pt} was - 0.233 V and the pH was 6.8. At this point, 15 mL of a 10 mg/L As(V) stock were injected and allowed to mix to yield a concentration of 500 µg/L As(V). Next, 6 - 7 mL of reactor solution were removed with a 10-mL plastic syringe and needle, placed in a 7.4-ml glass vial, and centrifuged (International Clinical Centrifuge, Model CL). The sample was then filtered by transferring it back to the syringe which was connected to a 25-mm filter holder containing a 0.65-µm filter (polyvinylidene fluoride, Millipore DVPP-047-00). Next, duplicate As(III)/As(V) separations were performed with the resin technique (Table 2.9) with 2-mL sample volumes. A portion of the sample (~1 mL) was not used in the separation process, but it was left in the sample vial to be used for determination of total arsenic prior to separation.

Samples were taken every 24 hr for the next 144 hr. A deaerated solution containing 5 mM $CaCl_2$ and 1 mM NH_4Cl was added as necessary to keep the level of water in the reactor constant. After the first five days, E_{Pt} and pH remained relatively constant. At 150 hr, a vacuum was applied at one of the arms and air was pulled through the reactor by uncapping the other arm. The As speciation was determined as above for the next 60 hr.

2.2.6 Controlled Reactor/Arsenic Study

A reactor system was developed in our laboratory by Lemmon for studying environmental redox transformations (24). The system is schematically illustrated in Figure 2.5. The system consists of a 2-L glass bioreactor, glass pH electrode, reference electrode (Ag/AgCl), Pt (E_{Pt}) electrode, dispensing pumps, a gas control system, and two external flow loops. The primary loop (A) contains a peristaltic pump and cross-flow filter for providing filtered solution for the secondary loop. The secondary loop (B) includes a piston pump, dissolved oxygen (DO) probe in a flow cell, a spectrophotometer flow cell, and a 3-way valve for obtaining filtered samples for external analysis. The spectrophotometer flow cell is positioned in the sample holder of a diode array spectrophotometer (Hewlett-Packard 8452A).

The system is capable of both monitoring and controlling parameters such as E_{Pt} and pH through the use of the dispense pumps which are controlled with a personal computer. Pumps are used to add small volumes of reagents (i.e.,oxidant or reductant) in a controlled mode to perform redox titrations or in a feedback mode to adjust or maintain the pH and E_{Pt} at specific values. The pH is adjusted or maintained by small additions of acid or base, while E_{Pt} is adjusted or maintained by addition of oxidizing or reducing agents or by changing the composition of gas introduced into the reactor.

The spectrophotometer is used to measure the absorbance of an immobilized redox indicator, in this case thionine. The indicator is immobilized on agarose beads (Spectra/Gel MAS beads) and these are packed into a flow cell with a 1-mm path length. The redox potential calculated from the absorbance of the oxidized form of the indicator is

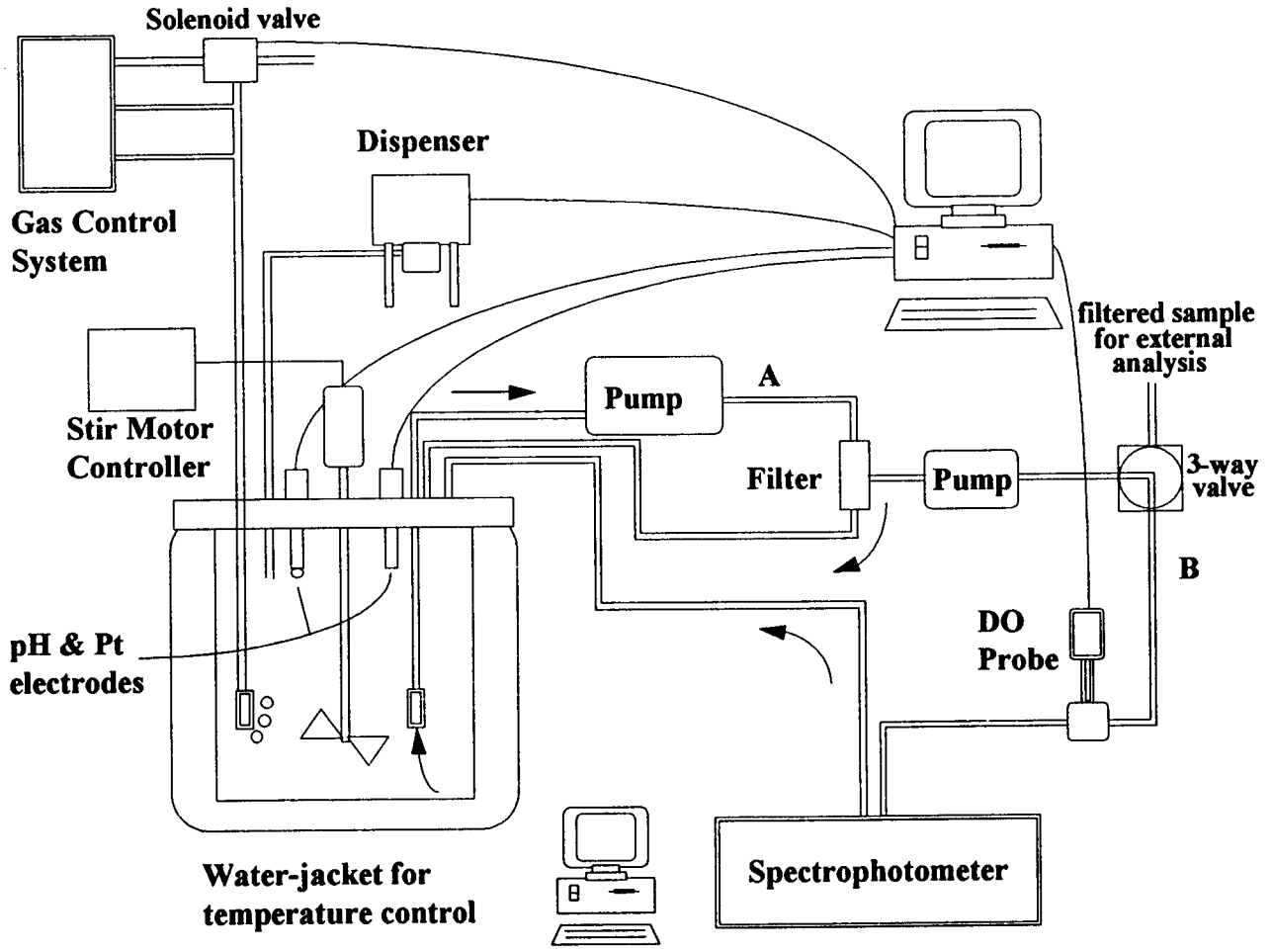


Figure 2.5 Controlled Reactor System. Taken with permission from reference 24.

then correlated to E_{Pt}. With this system, a study of the redox transformations of arsenic was conducted with the goal of correlating changes in E_{Pt}, Fe(II) concentration, or indicator speciation or absorbance with a change in arsenic speciation.

Bashaw A1 soil was taken and sieved to 2-mm mesh. This 2-mm mesh fraction was further sieved to 0.5-mm mesh. The 0.5-mm mesh fraction was then sieved further to 0.2-mm mesh. Approximately 50 g of the 0.2-mm mesh Bashaw A1 soil were added to 1 L of DI H_2O in the reactor along with 0.74 g of $CaCl_2$ and 0.05 g of NH_4Cl to yield concentrations of 5 mM and 1 mM, respectively. Next, 500 µL of a 1000 mg/L As(V) solution were injected into the reactor. The reactor was sealed and the N_2 purge was started. The slurry was mixed and 6 - 7 mL of sample were removed with a 10-mL plastic syringe attached to a piece of Peak tubing (Upchurch) which was inserted into the reactor for the purpose of sample removal. The sample was centrifuged and filtered through a 0.65-µm filter (polyvinylidene fluoride, Millipore DVPP-047-00) in a 25-mm filter holder as described in section 2.2.5. Next, duplicate As(III)/As(V) separations were performed with the resin technique (Table 2.9) with 2-mL sample volumes. Again, 1 mL of the sample was not used in the separation process but left in the sample vial for determination of total arsenic prior to separation.

Samples were periodically withdrawn and the speciation determined over the next 1300 hr. The pH and E_{Pt} were continually monitored and recorded. The pH was not maintained at a constant value but allowed to assume its natural value. The concentration of Fe(II) during the course of the experiment was determined by Brian Jones using the 1,10-phenanthrolene method (25). The absorbance of the immobilized indicator

was also recorded. A deaerated solution containing 5 mM $CaCl_2$ and 1 mM NH_4Cl was added as necessary to keep the level of water in the reactor constant.

After 600 hr, the solution in the reactor had reached reducing conditions (E_{Pt} = - 0.257 V), with total arsenic increasing slightly. The solution was then re-oxidized in a step-wise fashion to an E_{Pt} of 0.1 V by addition of 0.1 M H_2O_2. After the solution had reached this value of E_{Pt}, addition of peroxide was stopped and the solution in the reactor was allowed to reach reducing conditions once more.

2.2.7 Sutter Creek/Mini-Reactor Study

The speciation of arsenic in creek water, at Sutter Creek, Ca., was determined in the field with the final disk separation technique (Table 2.9). Figure 2.6 shows the location of the site (49). The small creek flows through a suburb which is constructed on top of a mine tailing pile containing arsenic. The mine tailing pile is the result of a deep-shaft mining operation in the vicinity of the suburb. The tailing pile has been covered with about 2 ft of topsoil, but the topsoil has eroded away in several places. There is the possibility that arsenic may be leaching into the creek.

Three water samples were collected from the creek in 30-mL polyethylene bottles. All samples were gathered from the same location in the creek. The first sample was used for immediate analysis. The second sample was marked unpreserved, and the final sample was taken and preserved, according to a recommended technique (26), by adding 300 µL of 0.1% ascorbic acid to 30 mL of sample. The pH of the samples were measured (pH meter Oakton WD-35615 Series and glass combination pH electrode Model 35801-71

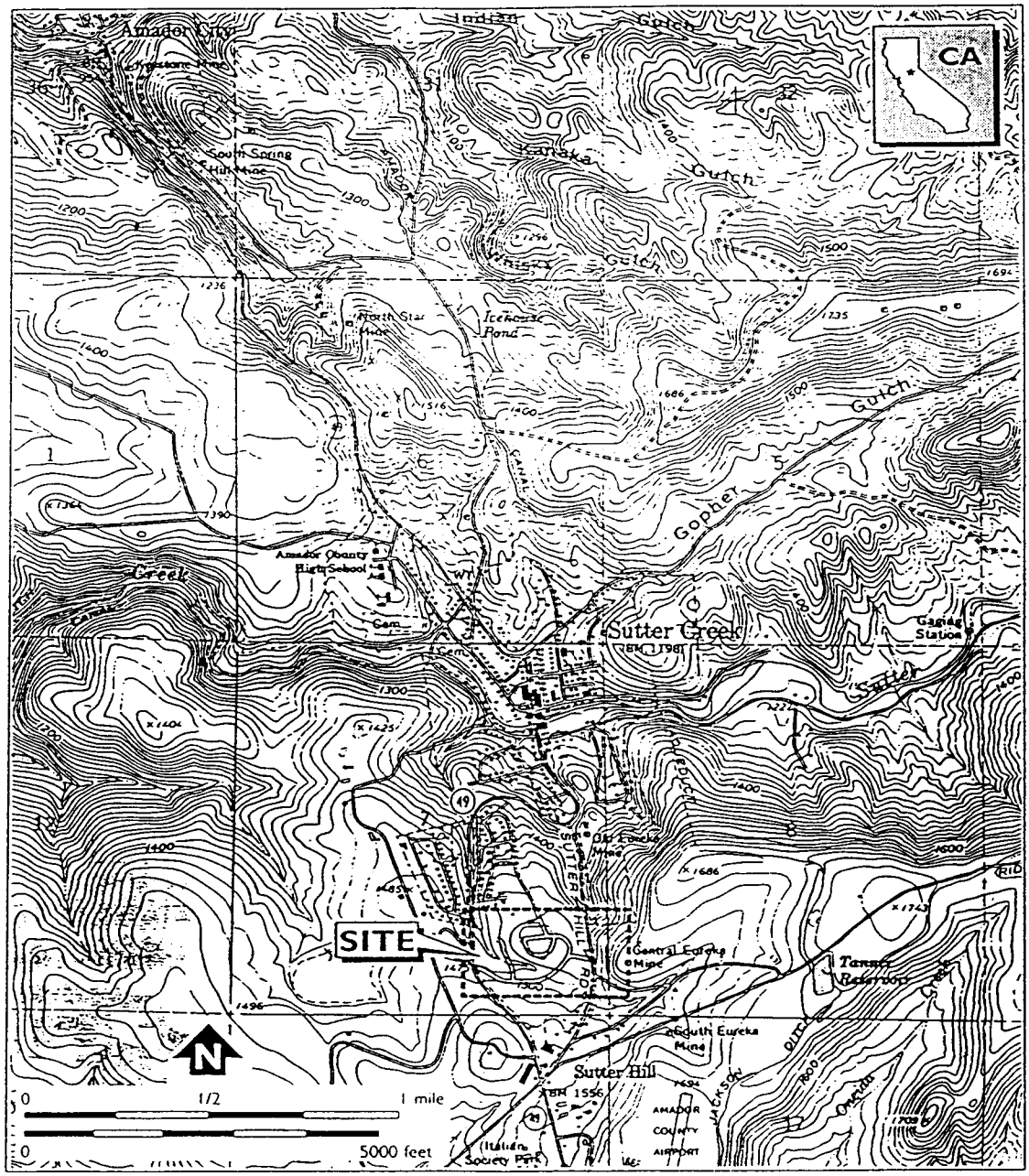


Figure 2.6 Site location map. Central Eureka Mine Site, Sutter Creek, Amador County, Ca. Taken without permission from reference 49.

AA5) after collection. A separation of the first sample was performed immediately in triplicate with 3-ml sample volumes according to the protocol in Table 2.9. Fractions were collected in 4-mL borosilicate vials and capped. A portable electric vacuum pump (VWR Scientific Model No. SA55NXGTD-4144) was used in conjunction with the vacuum manifold. Analysis by GFAAS of the As in the fractions as well as total As in the sample was performed approximately 24 hr later.

About 48 hr after collection, a triplicate separation was performed in the lab on the second and third samples followed by GFAAS analysis of the fractions. About 1 mL of each sample was saved and used for a total arsenic analysis.

A sample of the mine tailing soil from the Sutter Creek area was collected in a plastic Ziploc bag. The tailing soil was then used in an experiment similar in procedure to the mini-reactor study. Initially, 15 g of tailing soil were placed in the mini-reactor along with 300 mL of DI H_2O. Next, 0.22 g of $CaCl_2$, and 0.02 g of NH_4Cl were added to yield concentrations of 5 mM and 1 mM, respectively. The reactor was capped, the initial E_{Pt} and pH recorded, and the N_2 purge was started. Significant reduction of species in solution did not occur as evidenced by the small change in E_{Pt} over the course of four days. Apparently, the organic content of the tailing soil was too low to support microbial reduction processes over the 4-day period.

Therefore, 11.3 g of tailing soil and 3.7 g of Bashaw A1 soil were placed in the reactor. This situation approximates the tailing/topsoil situation present at Sutter Creek. Reagents such as DI H_2O, $CaCl_2$, and NH_4Cl were added to the reactor as before. The slurry was mixed, the N_2 purge was started, and the initial E_{Pt} and pH recorded. Periodically, 5 - 6 mL of sample were withdrawn with a 10-mL plastic syringe,

centrifuged, and filtered through a 25-mm filter holder containing a 0.65-μm filter (polyvinylidene fluoride, Millipore DVPP-047-00). Both E_{Pt} and pH were recorded at the time of sampling.

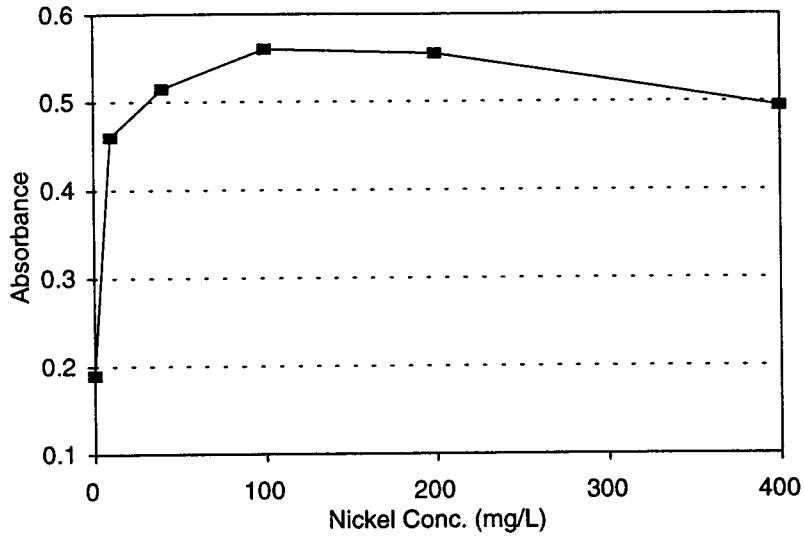
Separation of arsenic species was performed with the final resin technique (Table 2.9) with 2-mL sample volumes. A portion of the sample was retained in the sample vial for determination of total arsenic prior to separation. The water level in the reactor was kept constant by addition of a deaerated solution containing 5 mM $CaCl_2$ and 1 mM NH_4Cl as necessary. The reactor was not continuously stirred but stirred only at the time of sampling, which seemed to facilitate the attainment of reducing conditions in the reactor.

2.3 Results and Discussion

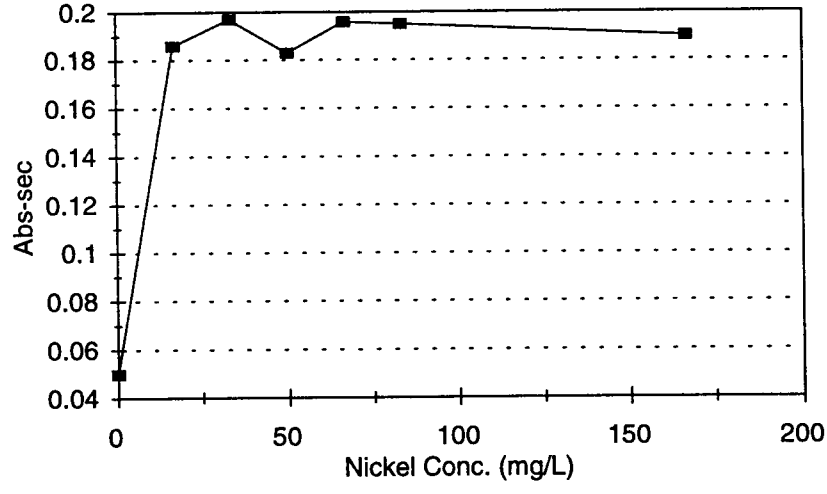
2.3.1 Nickel Matrix Modification and Calibration

Initially, the concentration of arsenic species was determined with a Varian AA-6 atomic absorption spectrophotometer. The instrument did not provide the detection limits and reproducibility ultimately required; however, it did aid in resolving the elution position of the two arsenic species. Results from these experiments also indicated that background correction was necessary to compensate for absorption by molecular species, such as sodium chloride, at the arsenic analytical wavelength of 193.7 nm. Eventually, all arsenic measurements were performed with a Perkin Elmer Zeeman/3030 spectrophotometer. It is a newer instrument and it provided the reproducibility, detection limits, and background correction required. The detection limit of 2 μg/L on the this instrument was determined as the concentration equal to 3 times the standard deviation, in concentration units, of five blank injections.

Nickel matrix modification was used in the determination of arsenic by GFAAS. The stabilization of arsenic by Ni in the furnace is well documented (27,28,29). The data for the optimization of the Ni concentration for both AA spectrophotometers are shown in Figure 2.7. The concentration of Ni in sample cup selected for further studies with the Varian and Perkin Elmer spectrophotometers was 83 mg/L and 80 mg/L, respectively. With a 20-μL injection size, this corresponds to roughly 2 μg Ni in the furnace. The typical amount of Ni recommended in the literature ranged from 2 to 20 μg (28,29). At low concentrations of Ni, loss of As in the ash step is significant. Once the concentration of Ni is sufficiently high, the exact amount of Ni to use is not crucial.



(a)



(b)

Figure 2.7 Optimization of Ni concentration in 1 mL of sample in sample cup. Matrix modification with Ni on: (a) Varian AA-6 spectrophotometer with an As concentration of 400 µg/L; (b) Perkin Elmer Zeeman/3030 spectrophotometer with As concentration of 50 µg/L.

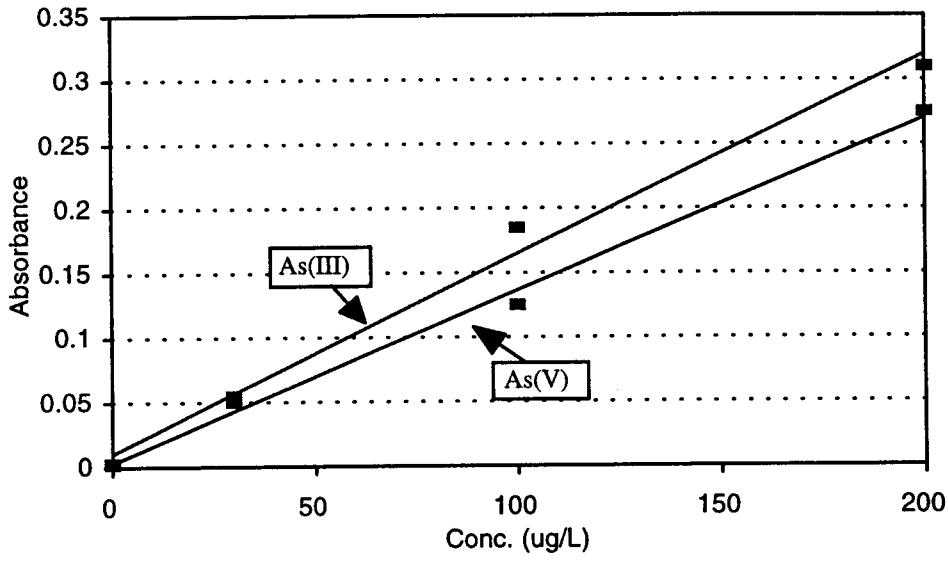
Separate calibration curves were constructed for As(III) and As(V). The calibration curves for both instruments are shown in Figure 2.8. The two oxidation states of arsenic were found to exhibit different sensitivities here as well as elsewhere (14,41). Presumably the difference in calibration slopes is a result of a difference in atomization efficiency between the two species. Standards of As(III) were prepared daily as significant oxidation of the As(III) was observed to occur over the course of a few days. Standards of As(V) were typically used for a week before fresh standards were prepared.

The detection limit for As with the Varian spectrophotometer is relatively poor (~20 μg/L). The detection limit could not be improved by increasing injection size because the size of the graphite furnace only permits injection of 10 μL samples. For the 100 μg/L standard solution, the peak height (in absorbance units) of the As(V) signal was 5 times greater on the Perkin Elmer spectrophotometer compared to that on the Varian spectrophotometer. The typical relative standard deviation on the Perkin Elmer instrument for a given 100 μg/L As standard was between 2 and 3%.

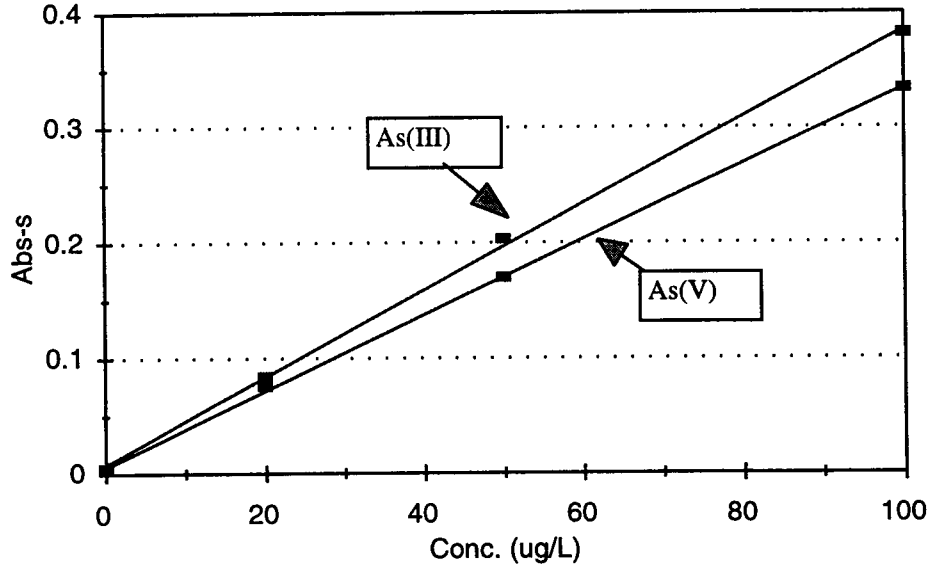
At one point in the experiments, preparation of arsenic samples in buffered solutions was tested. Phosphate buffer and various biochemical buffers such as, BIS-TRIS (Sigma), BES (Sigma), and MES (Sigma) were tested at the 0.01 M level. All buffers suppressed both As(III) and As(V) signals by at least 35%.

2.3.2 Optimization of the Conditioning and Separation Protocols

Initially, separation of arsenic species was performed with the resin protocol recommended by Ficklin (14) . This protocol did not work for two reasons:



(a)



(b)

Figure 2.8 Calibration curves for As(III) and As(V) with: (a) Varian AA-6 spectrophotometer (10 µL injection); (b) Perkin Elmer Zeeman/3030 spectrophotometer (20 µL injection).

1) acidification of samples to 0.12 M with HCl led to As(V) being unretained and 2) the use of HCl for the elution of As(III), as well as for sample acidification, led to the suppression of As(III) signals. Figure 2.9 illustrates the elution pattern of As(V) when the sample was acidified to 0.12 M with HCl. At this pH (<1), As(V) should be present as a neutral species and therefore be unretained. Retention of As(V) was improved by using a protocol which involved an initial cleaning step with alternating washes with 1 M HCl and 1 M NH_4OH and conditioning the resin with larger volumes of the conditioning solutions. By decreasing the amount of resin used and increasing the volume of conditioning solutions used, a more complete conversion to the acetate phase is achieved. Thus, the retention of As(V) is improved. It was later discovered, with the resin protocol in Table 2.9, that As(V) was retained in samples which were acidified to 0.01 M HCl. However, at a level of 0.1 M HCl, breakthroughs of 10 - 20% of the As(V) became a problem.

Figure 2.10 illustrates the effect of HCl on the As(III) signal. The figure illustrates what may happen if samples are acidified with HCl or when HCl is used as the only eluent for both species. Because of this phenomenon, HCl was never used for sample preservation and HCl was replaced by HAc, and eventually DI H_2O, as the eluent for As(III) in the second fraction. The suppression, shown in the figure, resulted from injecting 10 μL of concentrated HCl into the sample cup containing 1 mL of As(III) standard, which yields a final HCl concentration of 0.1 M in cup. Presumably, the suppression is the result of As(III) forming a more volatile arsenic trichloride which is lost in the dry or ash step. Interestingly, injection of Cl^- as the sodium salt did not suppress the As(III) signal, if the pH was near neutral. The magnitude of suppression was typically greater than 40% and was used as a qualitative test for the presence of As(III).

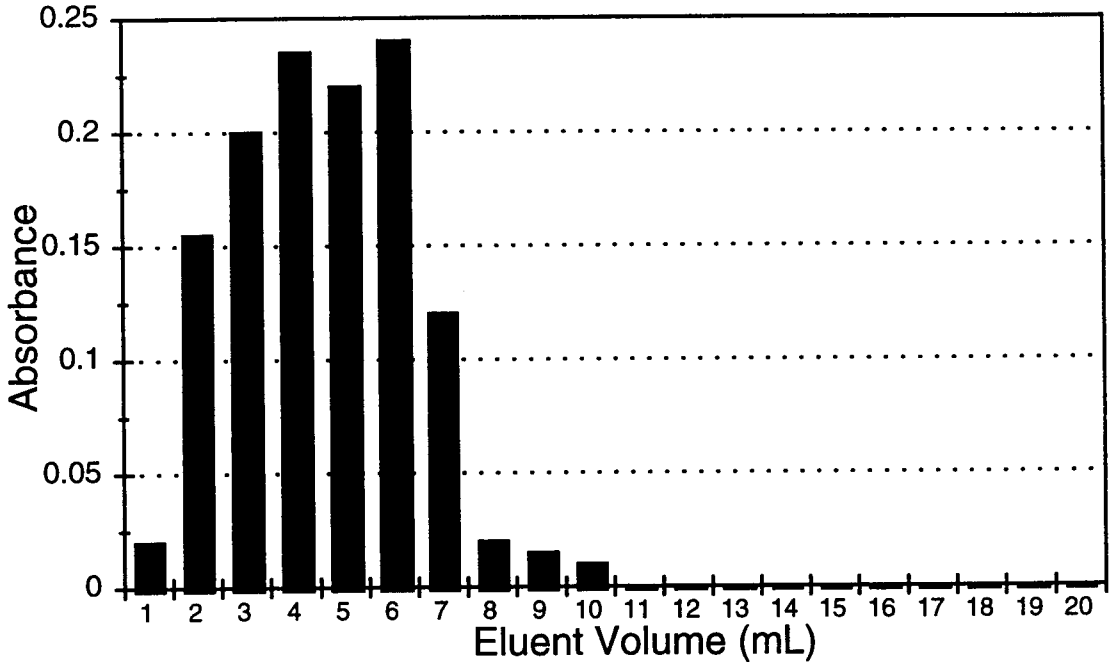


Figure 2.9 Elution pattern of a 5 mL sample of 0.5 mg/L As(V) in 0.12 M HCl. Protocol is that recommended by Ficklin (Table 2.8) with the 10 cm x 0.7 cm column packed with anion resin. According to Ficklin, As(V) started to elute after 13 mL of eluent.

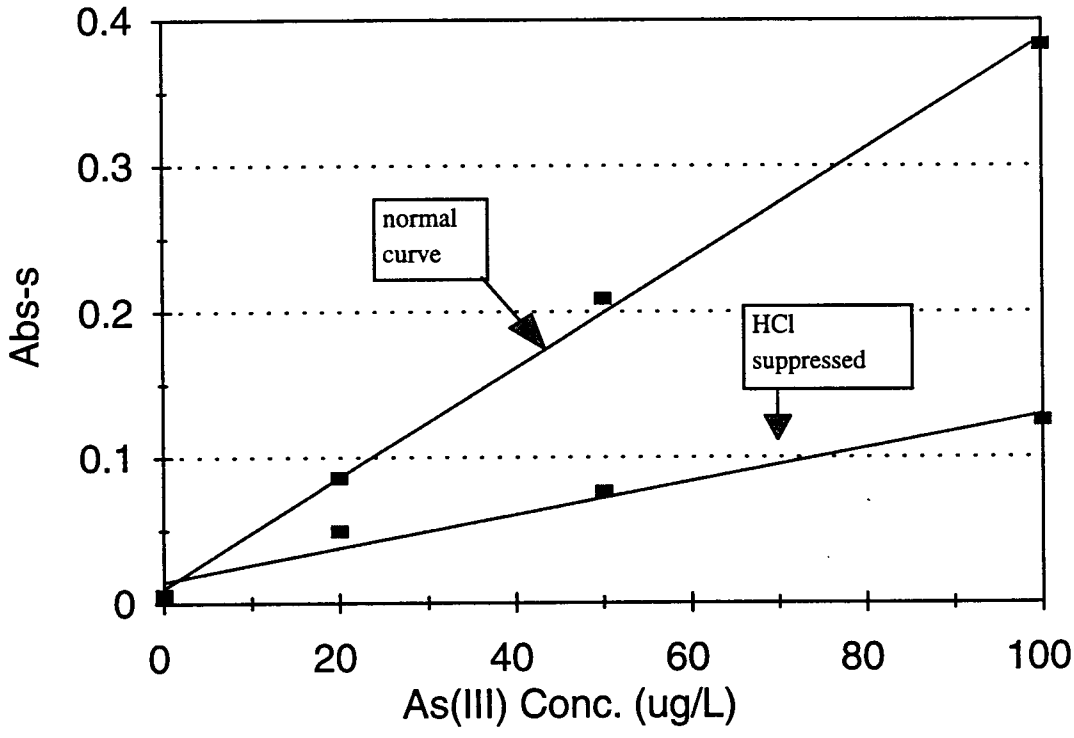
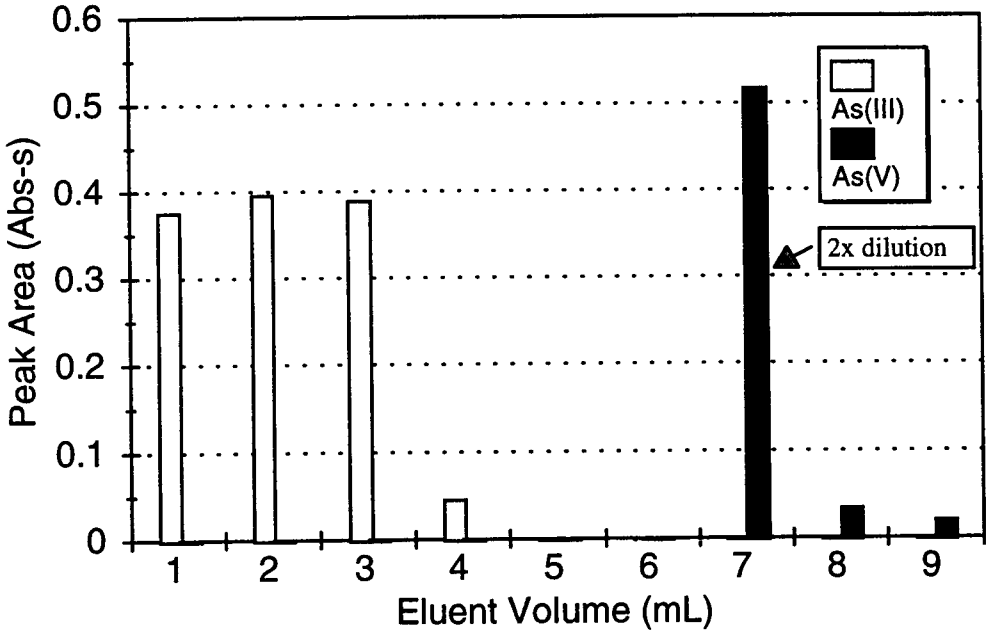


Figure 2.10 Suppression of As(III) standard signals by HCl. Suppression data obtained by injecting 10 µL of concentrated HCl into 1 mL of sample in GFAAS sample cup.

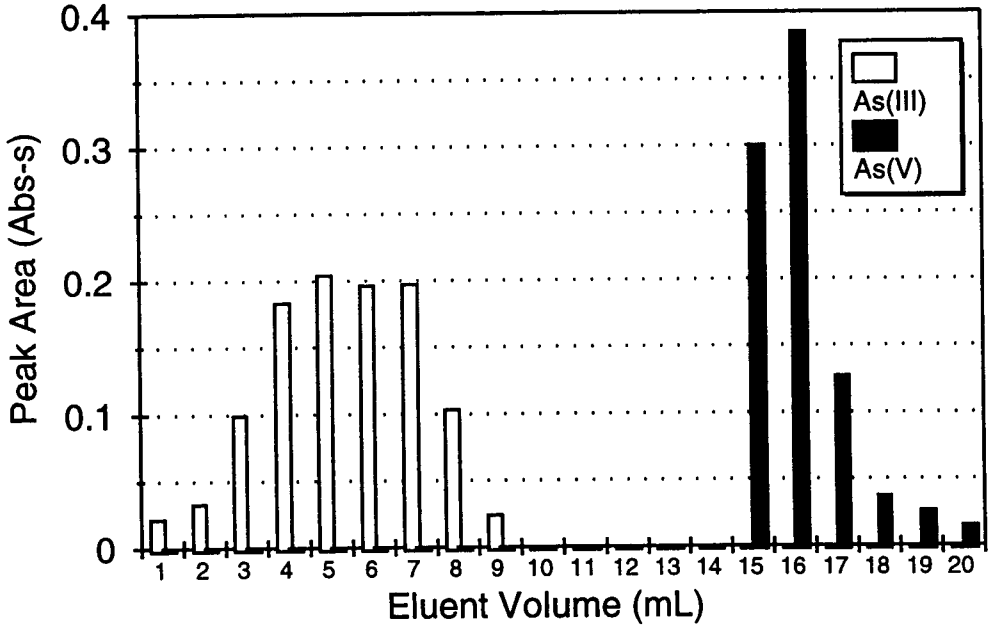
For example, if addition of HCl to a sample cup results in no change in the As signal, one can assume that the As in the sample is predominantly As(V).

At one point, the magnitude of the suppression effect decreased. Further investigations revealed that the age of the As(III) stock and the background matrix affected the magnitude of the suppression. The As(III) standards which displayed significantly suppressed signals (Figure 2.10) had been prepared in acetate buffer. To compensate for the possible effect of the background acetate, an alternate "suppressing solution" of 50% concentrated HAc and 50% concentrated HCl was prepared. This solution suppressed the As(III) signal equally if not more than concentrated HCl alone. With standards prepared from a relatively old 1000 mg/L stock, the suppression was only 10 - 15%; whereas, when standards were constructed from a freshly prepared 1000 mg/L stock solution, the suppression was greater than 50% for the 100 µg/L standard. The reason for the difference in the magnitude of the suppression between fresh and old standards is not fully understood.

Figure 2.11 displays the elution patterns for As(III) and As(V) obtained with anion-exchange resin and the anion-extraction disk with the final protocols listed in Table 2.9. The conditioning protocols are identical for both techniques. Compared to the disk technique, the resin method requires a larger volume of the 0.1 M HCl eluent for As(V) because of the larger bed volume. The sample volume can be varied based upon the application. During the course of experiments, sample sizes from 2 to 20 mL were used. For convenience, the volume of each fraction collected was equal to the sample volume used (for sample volumes between 2 to 5 mL). Thus, dilution factors did not have to be applied.



(a)



(b)

Figure 2.11 Elution patterns of 0.1 mg/L As(III) and 0.1 mg/L As(V) with: (a) disk method; (b) resin method. Data obtained with the protocols listed in Table 2.9 with a 3-mL sample size for disk and a 5-mL sample size for resin.

With the disk technique, the two arsenic species elute faster and in a smaller total volume of eluent and therefore fewer fractions need to be collected. However, with the disk technique, arsenic samples must be adjusted to pH 7 - 8 to convert the As(V) to the divalent anion ($HAsO_4^{2-}$) to enhance retention and prevent the breakthrough of As(V). With the resin technique, this pH adjustment is not necessary and a sample pH as low as 2.5 is acceptable. With both techniques, sufficient conversion to the acetate form of the resin is critical in achieving separation between As(III) and As(V). If the resin, or especially the disk, is not sufficiently converted to the acetate form, As(V) tends to breakthrough.

The percent recoveries for both the disk and resin technique are compared in Table 2.10. At the 98% confidence level, there is no significant difference between the two techniques in the percent recovery of As(III) and As(V). In addition, Figure 2.12 illustrates the results of a recovery study with the disk technique of As(III) and As(V) from seven different solutions containing various ratios of As(III) and As(V). The recovery of both As(III) and As(V) appears quantitative (within 5 µg/L of the expected value) for the concentration range of 0 to 100 µg/L.

2.3.3 Applications of the Extraction Disks

The Empore strong anion-extraction disks are a relatively new product. These disks are constructed out of PTFE and are impregnated with a strong anion-exchange resin similar to the Dowex 1x8. A main advantage of the disk is that the dense packing and uniform distribution of the adsorbent particles decreases the potential for channeling which

Table 2.10 Percent Recoveries for Resin and Disk Techniques

Technique	**Resin** [a]			**Disk** [b]		
	As(III)	As(V)	mix[c]	As(III)	As(V)	mix[c]
Mean % recovery	95	99	95 : 98	99	96	98 : 97
Absolute SD (n = 5)	2	2	1 : 2	3	2	1 : 1

[a] For the resin technique, the As concentrations measured in the first two fractions are added together to give total As(III). Total As(V) is calculated by adding the concentrations of the last two fraction together.

[b] For the disk method, total As(III) is calculated in the same manner as for the resin technique, but total As(V) is simply equal to the concentration measured in the last fraction.

[c] A solution of 100 µg/L As(III) and 100 µg/L As(V).

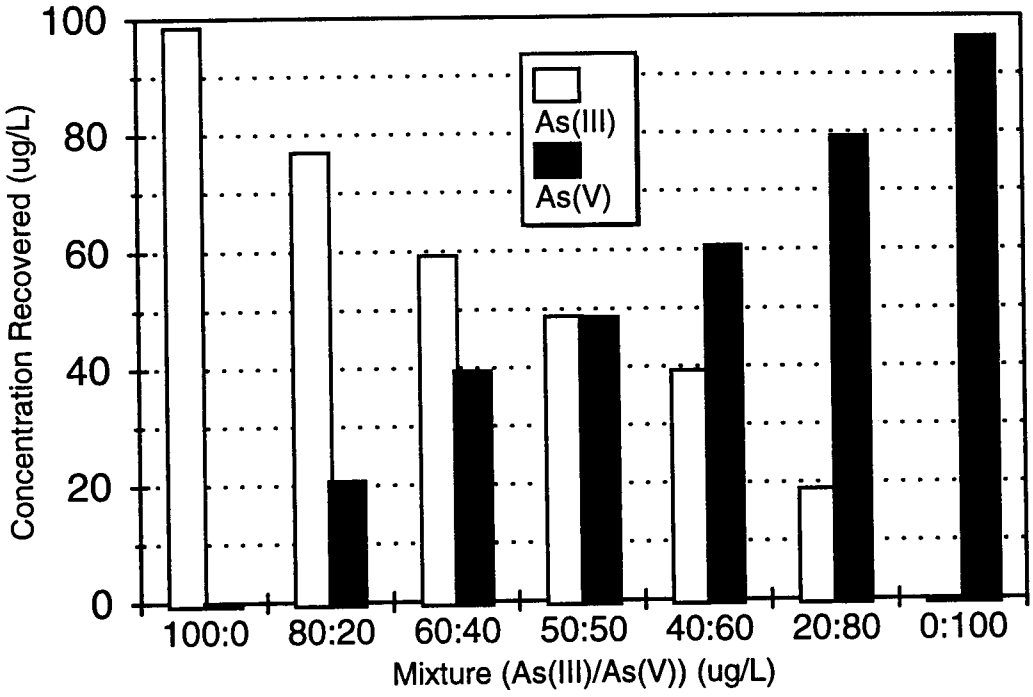


Figure 2.12 Recovery of arsenic from seven solutions with various concentration ratios of As(III) and As(V). Separation performed with the disk technique with the protocol listed in Table 2.9 and a 3-mL sample size.

may occur with a column of resin. In addition, because of the lower bed volume of the disks, smaller eluent volumes are needed thereby decreasing the time required for separation. To our knowledge, this application is the first use of these disks for the separation of arsenic species. The disks were used in the study of the oxidation of As(III) with time, in experiments preconcentrating As(V) in solutions with As(V) at or below the detection limit, and finally for the in-field separation of As species at Sutter Creek, Ca.

Figure 2.13 illustrates the oxidation of a 100 μg/L As(III) standard stored in either a Pyrex volumetric flask or a 4-mL borosilicate sample vials. The oxidation of As(III) in aqueous solution has been a contested subject. Both Crecilius et. al. (30) and Feldman (31) found that As(III) was oxidized in deionized water, while Tallman and Shaikh (32) reported that aqueous solutions containing As(III) at the μg/L level could be stored in Pyrex glass containers for 3 weeks without significant conversion to As(V). As can be seen from Figure 2.13, almost 40% of the As(III) in the flask was oxidized to As(V) within 3 days. The extent of oxidation of As(III) was less in the vial but still significant (10% in 3 days).

The more extensive oxidation in the flask might be due to the larger headspace in the flask (50 - 60 mL) compared to that in the vial (roughly 0.5 mL). Hence, there was a larger "sink" of O_2 in the flask as a result of the larger headspace. The more extensive oxidation in the flask may also be a result of the type of container used (i.e., borosilicate glass vs. Pyrex) or the growth of microorganisms in the flask that are capable of oxidizing As(III) (2).

The effect of the competing anions, chloride and nitrate, on the retention of As(V) with the extraction disks was investigated. Figure 2.14 illustrates the effect of these anions on

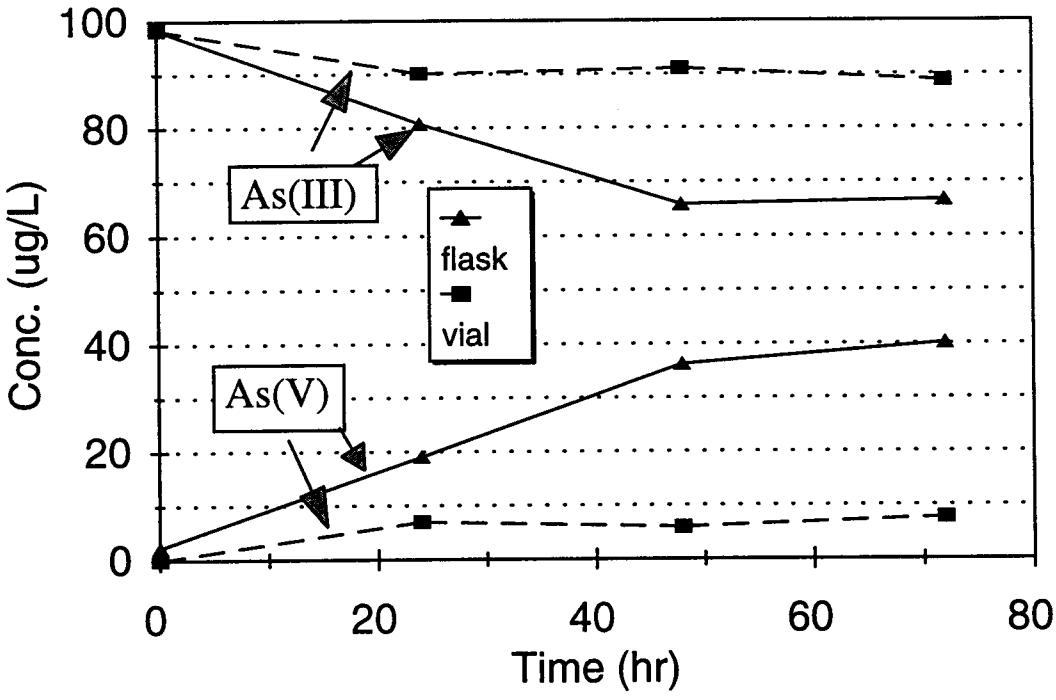
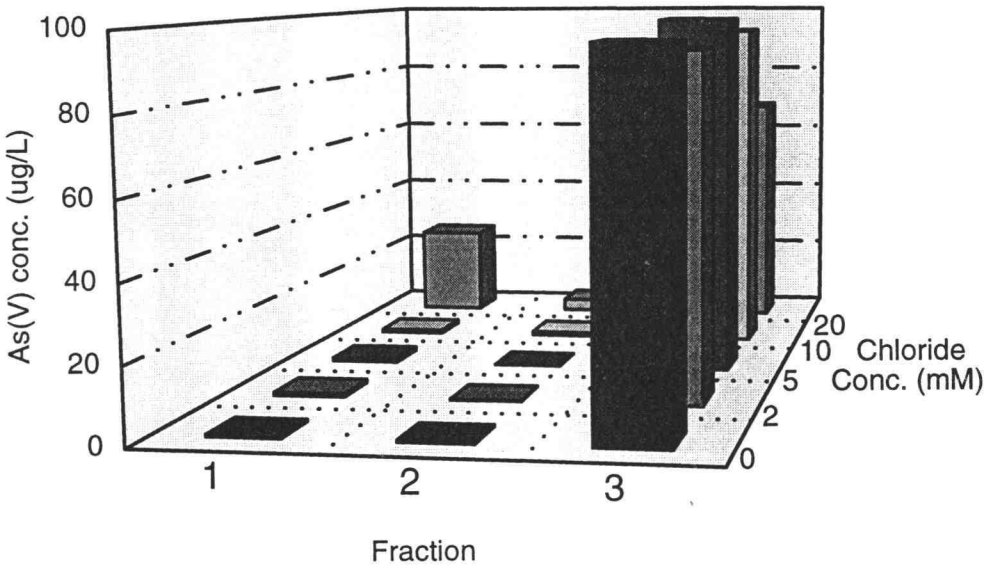
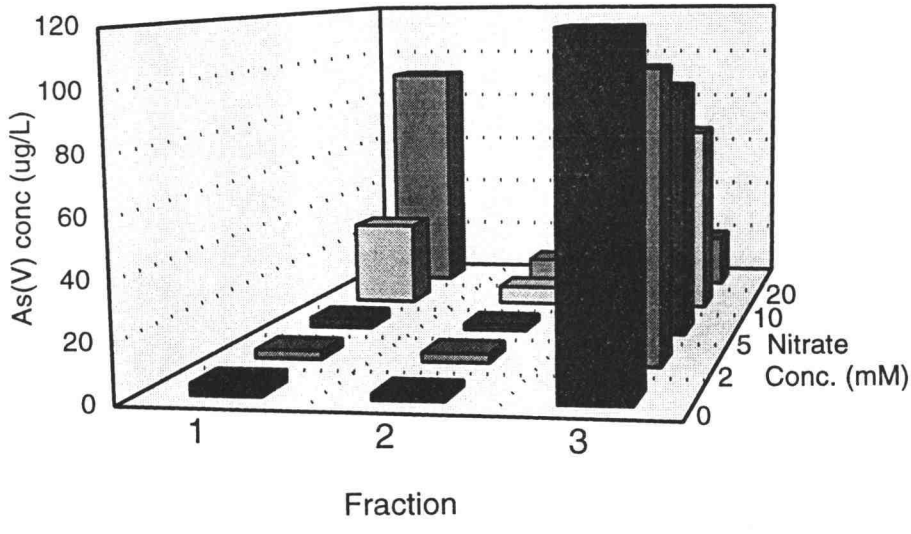


Figure 2.13 Oxidation of 100 µg/L As(III) in a 100-mL Pyrex volumetric flask and a 4-mL borosilicate sample vial.



(a)



(b)

Figure 2.14 Effect of (a) Cl^- and (b) NO_3^- on the retention of 100 µg/L As(V) by the anion-extraction disk. Data obtained with protocol listed in Table 2.9 with a 3-mL sample size.

the elution position of As(V). For chloride, a concentration of 20 mM results in a 20% breakthrough of As(V); whereas for nitrate, a concentration of 10 mM results in over 20% breakthrough. Both the Cl^- and NO_3^- successfully compete for the sites at a high enough concentration. The breakthrough of As(V) as a result of the insufficient capacity of the disk resulted in the resin separation technique being used for the remainder of the experiments except for the in-field separation of As species at Sutter Creek. However, the disks are suitable for determination of arsenic speciation in most groundwaters where typical Cl^- and NO_3^- concentrations are 1 mM or less (53,54).

A promising application of the disks is for preconcentration of As(V) in samples containing levels of As(V) at or below the normal detection limit, assuming of course, a low background concentration of competing anions. Table 2.11 lists the results of preconcentrating As(V) at the 1 and 10 µg/L level from either a 2- or 20-mL sample. The As(V) present in the 2- or 20-mL sample is preconcentrated on the disk and then eluted into a 3-mL fraction. The corrected concentration is the measured concentration multiplied by either 3/2 or 3/20. With a larger sample volume, 10 µg/L As(V) can be determined with better accuracy and 1 µg/L As (V) can be detected. However, the latter value reported in the table for the 1 µg/L sample is double that expected. This error may be due to As(V) contamination in the flask in which the 1 µg/L standard solution was prepared and stored.

Table 2.11 Preconcentration of Low-levels of As(V) with Extraction Disks

Sample Vol.[a] (mL)	As(V) Conc.[b] (µg/L)	Frac #3 Conc.[c] (µg/L)	Corrected Conc. (µg/L)
2	1	n/d	-------
2	10	8 (1)[f]	12 (1)[d]
20	1	11 (1)	2 (0.1)[e]
20	10	67 (8)	10 (1)[e]

[a] 2 or 20 mL sample volumes were used, followed by 3 mL of DI H_2O, followed by 3 mL of 0.1 M HCl.

[b] Concentration of As(V) in standard used in the experiment.

[c] Represents concentration of As(V) measured in the third fraction.

[d] A dilution factor of 3/2 is used because 2 mL of sample was placed on column and As(V) was collected in 3 mL of eluant.

[e] A dilution factor of 3/20 is used because 20 mL of sample was placed on column and As(V) was collected in 3 mL of eluant.

[f] Standard deviation, in parenthesis, calculated from average concentrations measured in duplicate runs (n = 2). Average concentrations were obtained from duplicate injections of each solution.

2.3.4 Redox Behavior of As in Laboratory Studies

The resin speciation technique was used in studying arsenic speciation when either As(III) or As(V) was combined with redox-active substances. Table 2.12 lists the results of this study.

The extent of oxidation of As(III) by dissolved oxygen over 24 hr was on the order of 5% at both pH 7 and 8 and is similar to that observed in the sample vial in the study of As(III) oxidation with the disk method. At pH 8, more soluble As(V) was detected at 0 hr than at 24 hr; however, this behavior was not observed at pH 7. Therefore, it is possible that there was a slight As(V) contamination at pH 8.

The extent of oxidation of As(III) by hydrogen peroxide was greater than that for dissolved oxygen. The concentration of oxidant was greater in the case of H_2O_2 (~0.6 mM vs. ~0.2 mM). With the H_2O_2 sample, some arsenic contamination may have occurred during the separation process as evidenced by over 100% recovery at 24 hr. Clearly, exposure of samples containing As(III) to O_2 or H_2O_2 must be prevented in order to avoid a change in the speciation between sample collection and analysis.

Oxidation of As(III) by manganese oxides has been observed previously (33). Here, significant oxidation of As(III) was seen immediately. At 24 hr, no As(III) was detected and the concentration of soluble As(V) previously detected at 0 hr had decreased. After oxidation of the As(III) to As(V), As(V) may be removed from solution by adsorption on the manganese oxide (34).

No As(III) was detected in solutions of As(V) reduced with Ti(III). The loss of As(V) from solution is attributed to adsorption of As(V) on Ti(IV) hydroxides which may have

Table 2.12 Summary of Arsenic Synthetic Redox Experiments

COMBINATIONS[a]	pH[d]	time (hr)	As(III) (µg/L)	As(V) (µg/L)	COMMENTS
As(III)/H_2O_2	5 - 6	0	91 (3)[e]	5 (1)	significant oxidation of As(III)
		24	40 (1)	75 (4)	
As(III)/O_2[b]	7	0	91 (4)	n/d[f]	slight oxidation of As(III)
		24	86 (2)	5 (1)	
As(III)/O_2[b]	8 - 8.5	0	91 (3)	10 (3)	slight oxidation of As(III)
		24	85 (3)	6 (2)	
As(III)/MnO_2[c]	8.5	0	3 (0.4)	60 (1)	significant oxidation of As(III) with adsorption of As(V)
		24	n/d	21 (3)	
As(V)/Titanium Citrate	2	0	n/d	44 (3)	no detectable reduction of As(V)
		24	n/d	45 (1)	
As(V)/ascorbic acid	6.5	0	n/d	85 (4)	no detectable reduction of As(V)
		24	n/d	91 (10)	
As(V)/Fe(II)	4 - 4.5	0	24 (1)	36 (1)	reduction of As(V) with possible re-oxidation after 24 hr
		24	n/d	54 (2)	
As(V)/Fe(II)	6.5 - 7	0	7 (1)	67 (7)	slight reduction of As(V) with complete adsorption after 24 hr, compare with pH 4 - 4.5
		24	n/d	n/d	

Table 2.12 Cont.

COMBINATIONS	pH	time (hr)	As(III) (µg/L)	As(V) (µg/L)	COMMENTS
As(V)/Fe(II)/aerate/ascorbic acid	6.5 - 7	0	39 (1)	5 (0.3)	reduction of As(V) with possible re-oxidation after 24 hr
		24	6 (1)	27 (1)	
As(V)/deaerate/Fe(II)/ascorbic acid/ deaerate	6.5 - 7	0	7 (1)	83 (7)	slight reduction of As(V) with adsorption after 24 hr
		24	4 (0.2)	48 (2)	
As(V)/ascorbic acid/deaerate/Fe(II)	6.5 - 7	0	n/d	70 (12)	no detectable reduction of As(V)
		24	n/d	54 (10)	
As(V)/deaerate/ascorbic acid/Fe(II)/ deaerate	6.5 - 7	0	n/d	91 (4)	no detectable reduction of As(V) but adsorption after 24 hr
		24	n/d	63 (5)	
As(V)/Fe(III)/ascorbic acid	6.5 - 7	0	4 (1)	74 (5)	slight reduction but significant adsorption
		24	3 (0.1)	56 (11)	
As(V)/Thionine/Fe(II)	6.5 - 7	0	51 (11)	16 (0.3)	large deviation in As(III) between duplicates
		24	7 (1)	10 (1)	

[a] Final concentration of components in solution: 100 µg/L As(III) or As(V), 0.125 mM $Fe(ClO_4)_2$ or $Fe(NO_3)_3$, 0.01% ascorbic acid (57 µM), 94 µM titanium citrate, 0.63 mM H_2O_2, 10 µM thionine.

[b] Experiment involved aerating 100 µg/L solution of As(III) by pulling air through solution with vacuum.

[c] Experiment involved combining 1 g synthetic birnessite with 20 mL of 100 µg/L As(III).

[d] pH was adjusted with 1 M HAc or 0.2 M NH_4OH.

[e] Standard deviations calculated from average concentrations measured in duplicate runs (n = 2).

[f] Not detected

formed in solution. The arsenic AA signal may also be suppressed in solutions of Ti(III) citrate, thus resulting in decreased concentration of arsenic detected.

Combinations of ascorbic acid with As(V) were investigated because As(V) was reduced to As(III) when ascorbic acid was used as a preservative for samples from Sutter Creek. However, as can be seen from Table 2.12, no reduction of As(V) to As(III) was observed after 24 hr.

The redox behavior of As(V) in the presence of Fe(II) was investigated next. At both pH 4 and 7, Fe(II) reduced As(V) to As(III). The reduction of As(V) by Fe(II) was generally rapid suggesting a homogenous reaction between the two species. After the reduction reaction, adsorption and coprecipitation processes most likely controlled soluble arsenic concentrations. Adsorption of arsenic is believed to occur through specific adsorption as opposed to purely electrostatic adsorption (37). Specific adsorption is a combination of ionic and non-ionic bonding interactions which can occur even at negatively-charged surfaces. Additionally, arsenate is more extensively adsorbed than arsenite (21,37,46,52). The adsorption of As(V) by Fe hydroxides is well documented (35,36,37). On amorphous iron hydroxides, maximum adsorption of As(V) and As(III) was found to occur at pH 4 and pH 7, respectively (37). Also, both As(III) and As(V) can coprecipitate with iron hydroxides (40). For a more extensive discussion, see Appendix A.

At time 0, the extent of As(V) reduction by Fe(II) was greatest at pH 4 as evidenced by a larger concentration of soluble As(III) and a lower concentration of soluble As(V). This behavior could be due to adsorption of a larger fraction of the As(V) on iron hydroxides at pH 4 as compared to pH 7. Additionally, the rate of reduction may be

greater at pH 4 compared to pH 7. At 24 hr, no As(III) was detected in solution at either pH possibly because of coprecipitation of the As(III) or re-oxidation of the As(III) by dissolved O_2 with subsequent adsorption or coprecipitation of the As(V). At 24 hr, no soluble As(V) was detected at pH 7; however, at pH 4, soluble As(V) was present. This behavior may be the result of more extensive coprecipitation of the As(V) at pH 7 as a result of the higher OH^- concentration.

Various combinations of As(V), Fe(II), Fe(III), and ascorbic acid were tested in attempts to duplicate the conditions for reduction of As(V) by ascorbic acid which occurred in the Sutter Creek samples. In both cases where As(V) and Fe(II) were combined before adding ascorbic acid, reduction of As(V) was observed at 0 hr. The most extensive reduction occurred in the sample that was aerated. This difference may be due to a pH effect. For the aerated sample, As(V) and Fe(II) were combined at pH 4 and then the sample was adjusted to pH 7; whereas for the deaerated sample, As(V) was combined with Fe(II) at pH 7. Again, the reduction at pH 4 may be kinetically faster compared to that at pH 7.

In the case denoted as As(V)/Fe(II)/aerate/ascorbic acid and in the case of As(V)/Fe(II) at pH 4, the reduction of As(V) by Fe(II) was apparently fast as evidenced by reduction of the As(V) even though the sample was aerated immediately in order to convert the Fe(II) to Fe(III). This behavior suggests a homogenous reduction reaction. Interestingly, the soluble As(V) concentration is larger after 24 hr as compared to 0 hr for both of these samples. Possibly, in these two samples, the larger amount of As(III) formed in the reduction of As(V) was re-oxidized by dissolved O_2, thus resulting in a greater concentration of soluble As(V) after 24 hr as compared to 0 hr. With all other

combinations of As(V), Fe(II), and ascorbic acid, the concentration of soluble As(V) was less after 24 hr compared to 0 hr possibly because of more extensive coprecipitation.

Combining As(V) and Fe(III) and then adding ascorbic acid resulted in detectable reduction of As(V). Again, soluble As(V) decreased after 24 hr as a result of adsorption. No As(III) was detected in solutions in which As(V) and ascorbic acid were combined before adding Fe(II) or Fe(III).

Reduction of As(V) was observed when As(V) was combined with the redox indicator thionine and Fe(II). However, there was a large variation in the concentration of soluble As(III) at 0 hr between duplicate runs. Possibly, the indicator interferes in the homogenous reduction reaction between As(V) and Fe(II). Thionine is reduced by Fe(II) in solution (24).

2.3.5 Mini-Reactor Study

The fate of 500 μg/L As(V) in a Bashaw soil slurry under reducing conditions in the Kontes mini-reactor (E_{pt} = -233 mV, pH = 6.8) is illustrated in Figure 2.15. Soon after its addition, only about 20% of the As(V) added was detected in solution. Presumably, the remaining 80% was adsorbed. Roughly 82% of total soluble arsenic (soluble As(III) + soluble As(V) = total soluble As) was As(V). However, within 24 hr, the soluble As(V) concentration decreased and the soluble As(III) concentration increased to 93% of total soluble arsenic. Reduction of As(V) to As(III) has been observed in the E_{Pt} range of 0 to -200 mV (10,40).

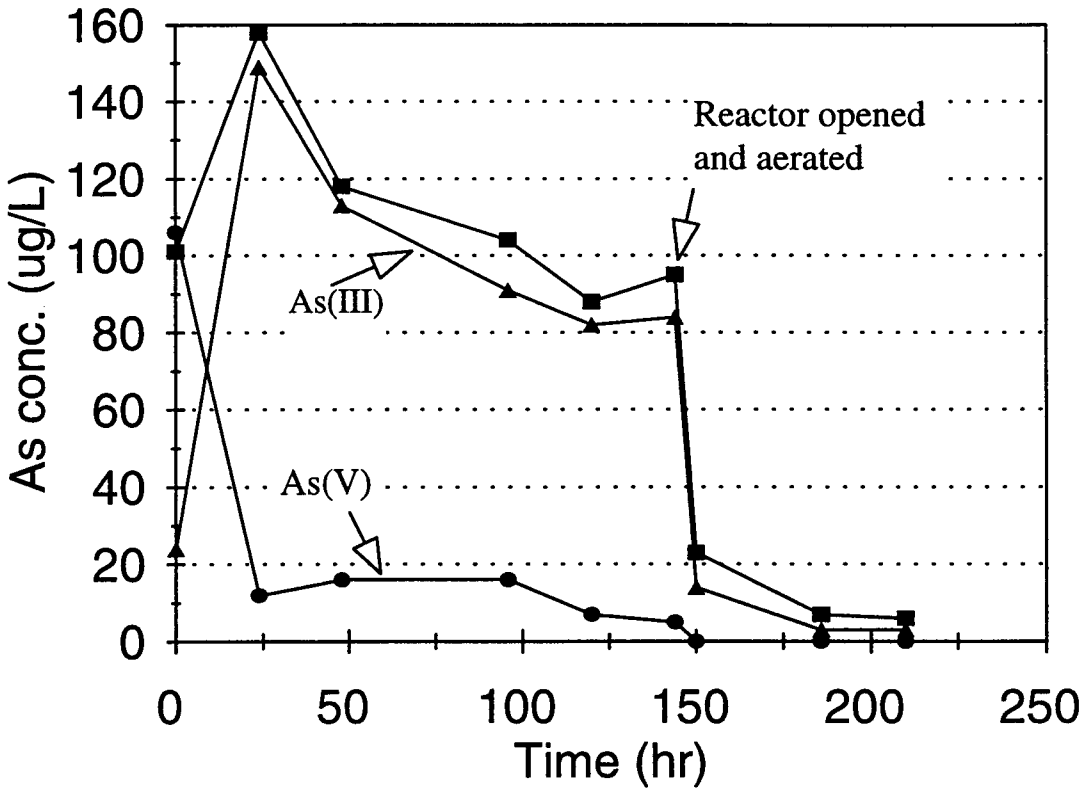


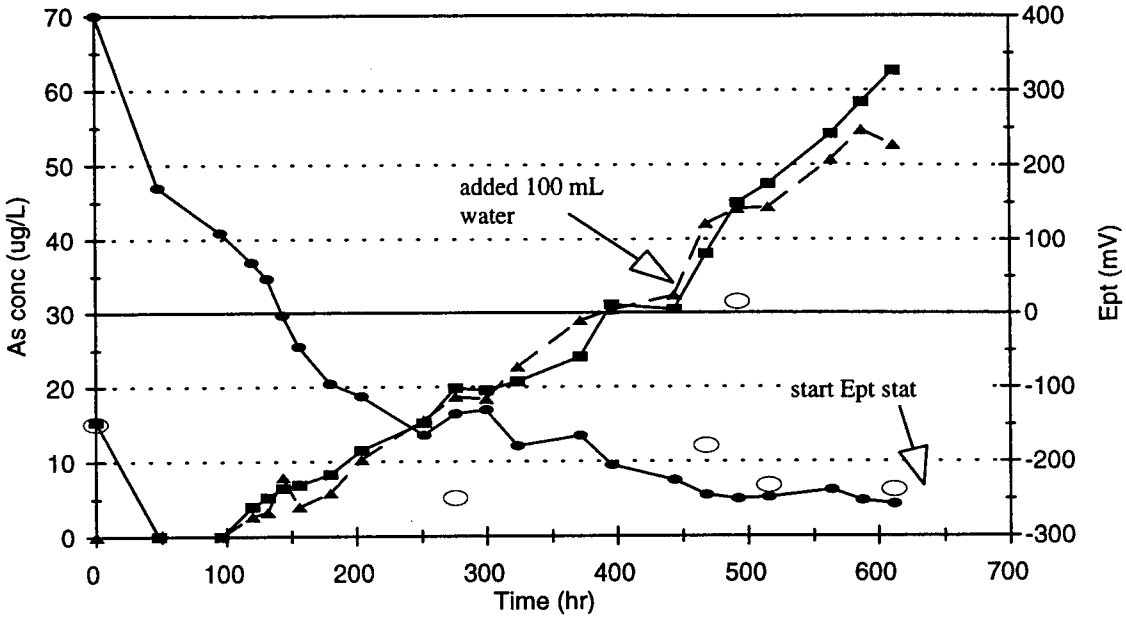
Figure 2.15 Arsenic speciation with time in a Bashaw soil slurry under reducing conditions. Soil slurry (15 g soil/300 mL H_2O) in reactor spiked to 500 µg/L As(V) at an E_{Pt} of -0.223 V and a pH of 7.54. Total As measured (■), As(III) (▲), and As(V) (●).

Over the next 120 hr, As(III) remained the predominate soluble arsenic species and the total arsenic concentration slowly decreased. Possible reasons for this decrease include the adsorption or coprecipitation of As(III) and the oxidation of As(III) with subsequent adsorption or coprecipitation of the As(V). It was also speculated that the decrease in arsenic concentration with time might be due a result of removing solution for analysis followed by addition of the deaerated salt solution to maintain a constant volume of solution in the reactor. However, calculations revealed that the sampling procedure had a negligible effect on the trend observed.

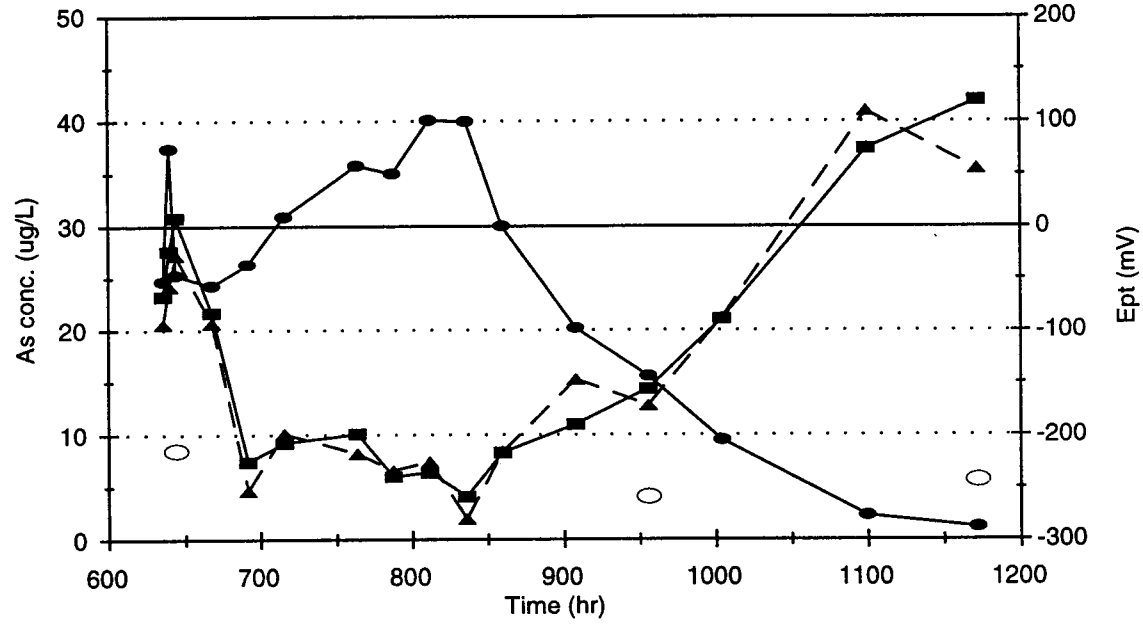
After 150 hr, the contents of the reactor were exposed to the air and the total arsenic concentration decreased to 6 μg/L within 210 hr, with As(III) being the only species detected. This study illustrates what may occur if As(V) were to be released into a reducing environment in a contamination scenario.

2.3.6 Controlled Reactor Study

The redox behavior of arsenic in a soil slurry was studied with a reactor system capable of monitoring and controlling both E_{Pt} and pH while simultaneously monitoring the absorbance of the redox indicator thionine. Figure 2.16 depicts the change in arsenic speciation, the concentration of total arsenic measured, and E_{Pt} over the course of the experiment. Figure 2.17 shows how the pH and E_{Pt} changed during the experiment as well as the relationships between E_{Pt} and the concentrations of total arsenic, As(V), and Fe(II) for the first 600 hr of the experiment. After the E_{Pt} control was initiated at 650 hr (addition of H_2O_2), the Fe(II) concentration fluctuated between 50 and 500 μM.

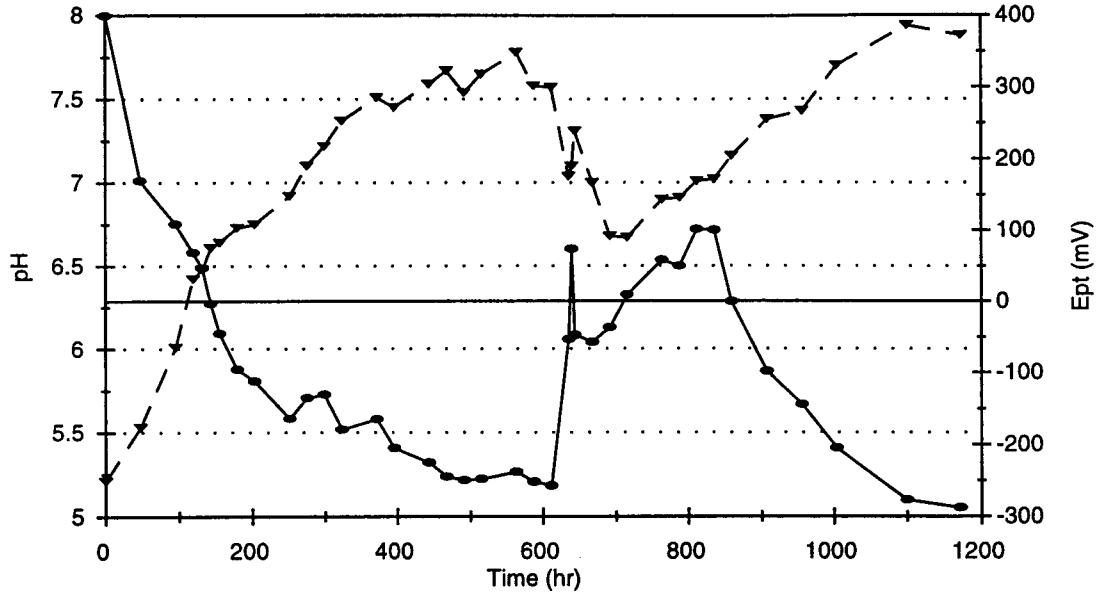


(a)

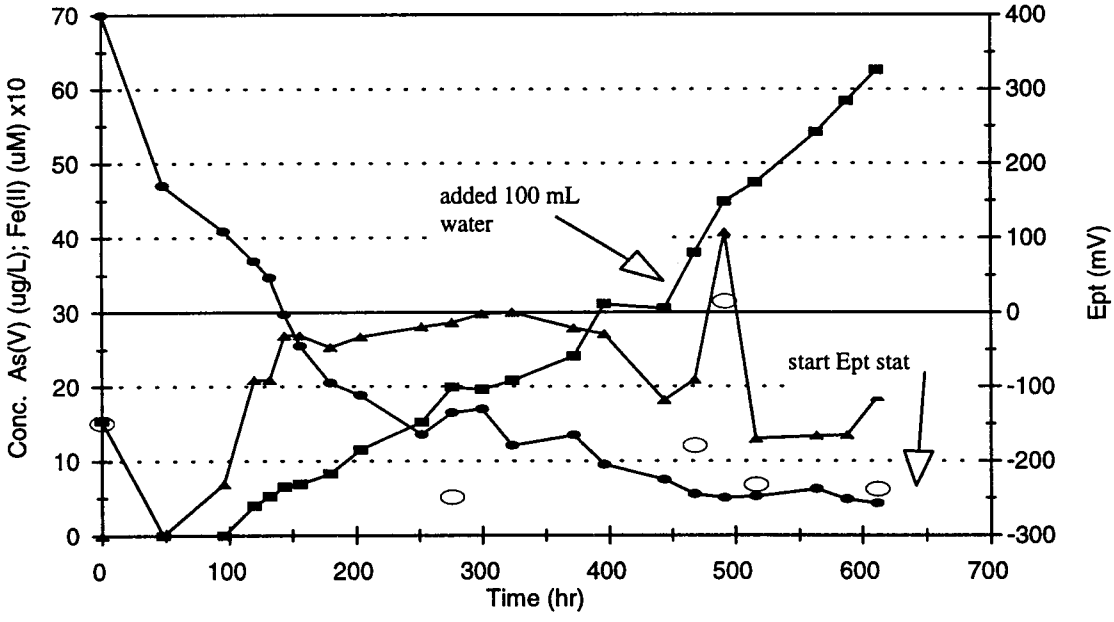


(b)

Figure 2.16 Arsenic speciation in the Bashaw soil slurry during the controlled reactor study. Total As (■), As(III) (▲), As(V) (○), and E_{Pt} (●) are shown as a function of time. (a) Before E_{Pt} stat; (b) after E_{Pt} stat (operable from 650 to 850 hr). Only points for As(V) levels above 4 µg/L are shown.



(a)



(b)

Figure 2.17 Time dependence of various properties in the Bashaw soil slurry during the controlled reactor experiment. (a) pH (▼) and E_{pt} (●) during experiment; (b) total arsenic measured (■), As(V) (○), E_{Pt} (●), and Fe(II) (▲) concentration during the first 600 hr.

This fluctuation may have been due to variations in the time interval between sampling for Fe(II) determination and H_2O_2 addition.

As can be seen in Figure 2.16a, total soluble As increased as E_{Pt} decreased because As(V) was reduced to the more soluble As(III) species. Arsenate was the only species detected immediately after injection. However, the soluble arsenic concentration soon became undetectable until 100 hr. Between 100 and 200 hr, the soluble As concentration increased as conditions became more reducing (0 to -100 mV), with As(III) being the only detectable species. Arsenite remained the predominant soluble species for the duration of the experiment. In As contaminated soil slurries at pH 5 to 7.5 (2.56 mg As/kg soil), Masscheleyn et al. (10,40) found that the total soluble As concentration increased in the E_{Pt} range of 0 to -200 mV with As(III) being the predominate species.

In the redox studies reported earlier, it was shown that Fe(II) effectively reduced As(V) to As(III) and that H_2O_2 oxidized As(III) to As(V). In the soil slurry, As(V) may have also acted as the electron acceptor and upon initiating the E_{Pt} stat by addition of H_2O_2 at 650 hr (Figure 2.16a), the total soluble As and As(III) concentrations decreased because of the oxidation of As(III) with subsequent adsorption of the As(V).

Several times during the course of the experiment, the sum of the As(III) and As(V) concentrations was greater than the total As measured by GFAAS. For example, at approximately 500 hr, total As was measured to be about 45 μg/L, with As(III) and As(V) concentrations of 44 μg/L and 31 μg/L, respectively. The disagreement between the value for total arsenic and the sum of the parts may be a result of the Fe(II) being oxidized to Fe(III) upon exposure to air, followed by adsorption or coprecipitation of the As(V) with these freshly-formed iron hydroxides. The aliquot of the sample which was used for the

total arsenic measurement was typically exposed to air 10 - 15 min longer than the aliquot of sample used for the separation. In separate experiments, it was shown that As(V) in the presence of Fe hydroxides was undetectable with GFAAS. The adsorption of As(V) by Fe hydroxides may have been less during the separation procedure because As(V) was effectively separated from Fe species before a significant amount of Fe hydroxides formed.

Figure 2.16b depicts the arsenic speciation with time upon initiating control of the E_{Pt}. The value of E_{Pt} was adjusted to 100 mV by addition of H_2O_2 in a step-wise fashion. The spike in E_{Pt} at around 650 hr was the result of the addition of too large a volume of H_2O_2. In general, as conditions became more oxidizing, total As decreased as a result of the oxidation of As(III) to As(V). As seen in the figure, when the slurry was allowed to reach reducing conditions a second time, total As increased because of the reduction of As(V) to the more mobile As(III).

As can be seen from Figure 2.17b, the As(V) and Fe(II) concentrations reached maxima after the addition of 100 to 200 mL of a deaerated solution containing 5 mM $CaCl_2$ and 1 mM NH_4Cl to the reactor at 450 hr. The soluble arsenic concentration also increased sharply (14 μg/L in 48 hr) at this time. A totally satisfactory explanation for these observations has still not been found; although, higher soluble As(V) concentrations as a result of the solubilization of the iron phase has been observed previously (40,45,46). The soluble As(V) concentration may have increased due to oxidation of soluble As(III) by O_2 in the salt solution added. However, this explanation is not consistent with the steady increase in soluble As(III) observed.

Another facet of this experiment involved trying to correlate a change in the speciation of the immobilized redox indicator thionine with a change in the arsenic speciation.

As shown in Figure 2.18, when E_{Pt} was between 0 and -100 mV and the pH was between 6.7 and 7 (100 to 200 hr), the soluble As(III) concentration began to increase and the indicator absorbance began to decrease. The indicator was 90% reduced after 350 hr when E_{Pt} was less than -150 mV. The As(III) concentration continued to increase long after the Fe(II) concentration and the indicator speciation had become somewhat stable. The Fe(II) concentration at this point was between 0.25 and 0.3 mM. In As contaminated soil slurries, Masscheleyn et al. (10) found that when the soluble As(III) concentration increased, the soluble Fe concentration was in the range between 1 and 2 mM. Lemmon (24) found that in experiments with a Bashaw soil slurry, which were performed at pH 6, the absorbance of the indicator began to decrease significantly when Fe(II) was between 0.4 and 0.5 mM for E_{Pt} between 100 and 0 mV.

The relationships among the Fe(II) concentration, pH, E_{Pt}, and the indicator absorbance are not yet fully understood. In addition, the effect of As on these parameters, as well as on microbial processes in the soil slurry, is not known. However, as can be seen from Figure 2.18, the immobilized thionine may be useful in a qualitative manner to predict which form of As (i.e., As(III) or As(V)) is predominant. The effect of maintaining the pH at a fixed value, as opposed to letting it vary and assume its natural value, is an important question in experimental design. Experiments have shown that at lower pH's (i.e., 6.0 - 6.3), a higher Fe(II) concentration is necessary to achieve reduction of the indicator in solution. At lower pH's, the indicator should be more easily reduced, but Fe(II) is not as effective as a reductant (47).

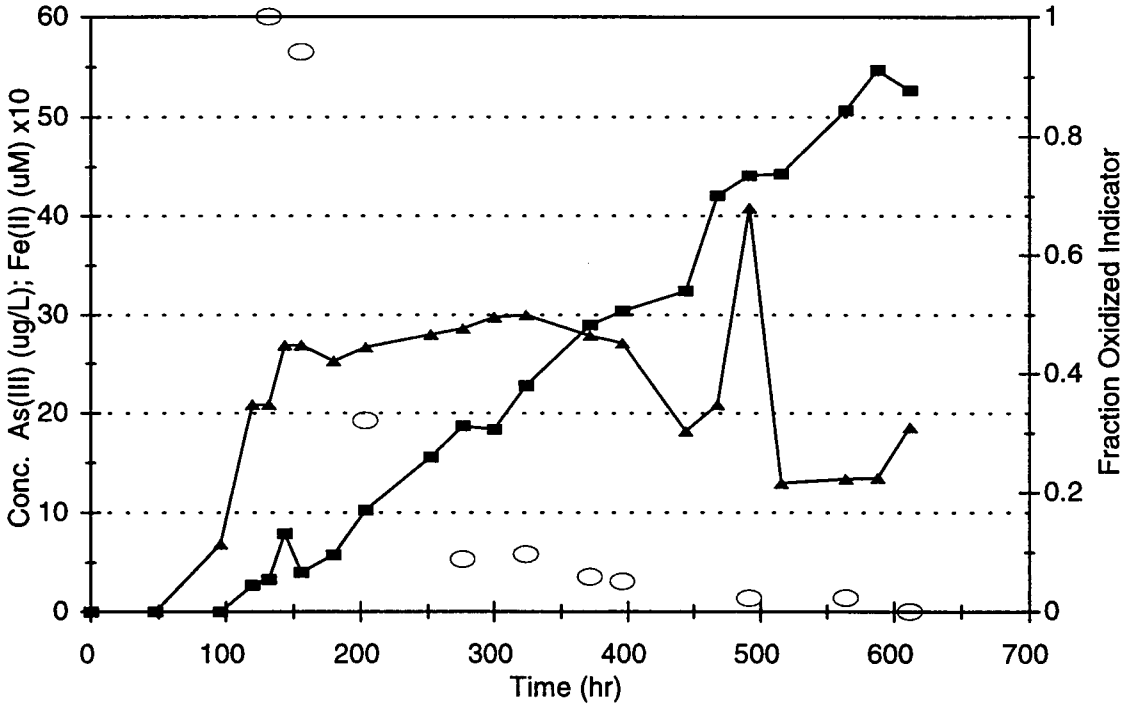


Figure 2.18 Behavior of immobilized thionine during the controlled reactor experiment with a Bashaw soil slurry. Fe(II) concentration (▲), fraction of oxidized thionine (○), and the As(III) concentration (■).

2.3.7 Sutter Creek

The disk speciation technique was applied in the field at Sutter Creek, Ca., where houses have been built on a mine tailing pile containing arsenic. Before construction began, quantitative measurement of arsenic were performed by the developer on soil grab samples from around the area. From these measurements, it was assumed that most of the arsenic was bound up as the mineral arsenopyrite (FeAsS) and therefore would not pose a health risk. For further protection, the pile was covered with 1-2 ft of topsoil. However, the topsoil continues to erode as a result of construction and natural weathering processes.

Analysis of soil samples from the area in 1994 by Seacor Analysis Corporation for the California Site Mitigation Unit of the Department of Toxic Substances Control showed a mean As content of 373 mg/kg with a background soil sample (unaffected by the tailings) containing 8.3 mg/kg (48). The tailings were enriched with arsenic by a factor of 45 compared to the background soil.

Sequential extraction results showed that a large fraction of the arsenic in the tailing soil (about 25% of total sample As) was sequentially extracted by distilled water, followed by magnesium chloride, and then a phosphate buffer solution (48). From this result, the researchers concluded that a large portion of the arsenic exists as water soluble and surface bound species which could be released depending on environmental conditions.

A small creek flows through the area of concern. The EPA Region IX Technical Assistance Team (TAT) measured a total As concentration of 13 μg/L in the creek during a heavy rain period in 1994 (49). During heavy rains, the mine tailings have been

observed eroding with runoff water. The creek also suffers from eroding banks. The TAT did not determine the arsenic speciation of the creek water.

Table 2.13 summarizes the results of determining the arsenic speciation in three samples collected from the same location in the creek. The first sample was immediately run through the separation process at the site and the AA analysis on the fractions was performed the next day. The second and third samples were collected and taken back to the laboratory for separation and analysis the following day. The second sample was not treated in any way, but the third sample was preserved with 1% ascorbic acid as recommended (26). The results show that As(V) was the only species detected in the first and second samples. The presence of only As(V) is not surprising as the creek was rather shallow and flowed across a coarse gravel bed which should keep the water well aerated.

The As(V) in the third sample treated with ascorbic acid was reduced to As(III). This behavior points out the problem one could encounter when sample preservation is required as is the case for many of the other As speciation methods which cannot be easily implemented on-site (e.g., hydride generation).

A sample of the tailing soil was also collected from the site. The As concentration was reported to be between 300 and 1200 mg/kg in this area, which was designated Mesa De Oro (MDO) 66,67 (49). The tailing soil was placed in the mini-reactor along with Bashaw A1 soil. This mixture roughly mimics the mixture of tailings/topsoil (tailing to topsoil weight ratio of 3 to 1) which occurs around the Mesa de Oro area. Figure 2.19 illustrates the changes in arsenic speciation with time during the experiment. Any effect of removing sample for analysis followed by addition of the deaerated salt solution to maintain a

Table 2.13 Determination of Arsenic Speciation in Creek Water

Sample	Total As (µg/L)[a]	As(III) (µg/L)[b]	As(V) (µg/L)[b]
immediate	8 (0.8)	n/d[c]	8 (0.4)
unpreserved	7 (0.2)	n/d	8 (0.3)
preserved	7 (0.8)	6 (0.4)	n/d

[a] Standard deviation from duplicate injections shown in parenthesis (n = 2).
[b] Standard deviations, in parenthesis, calculated from average concentrations measured in the triplicate runs (n = 3). The average concentration was obtained from duplicate injections of each solution.
[c] Not detected

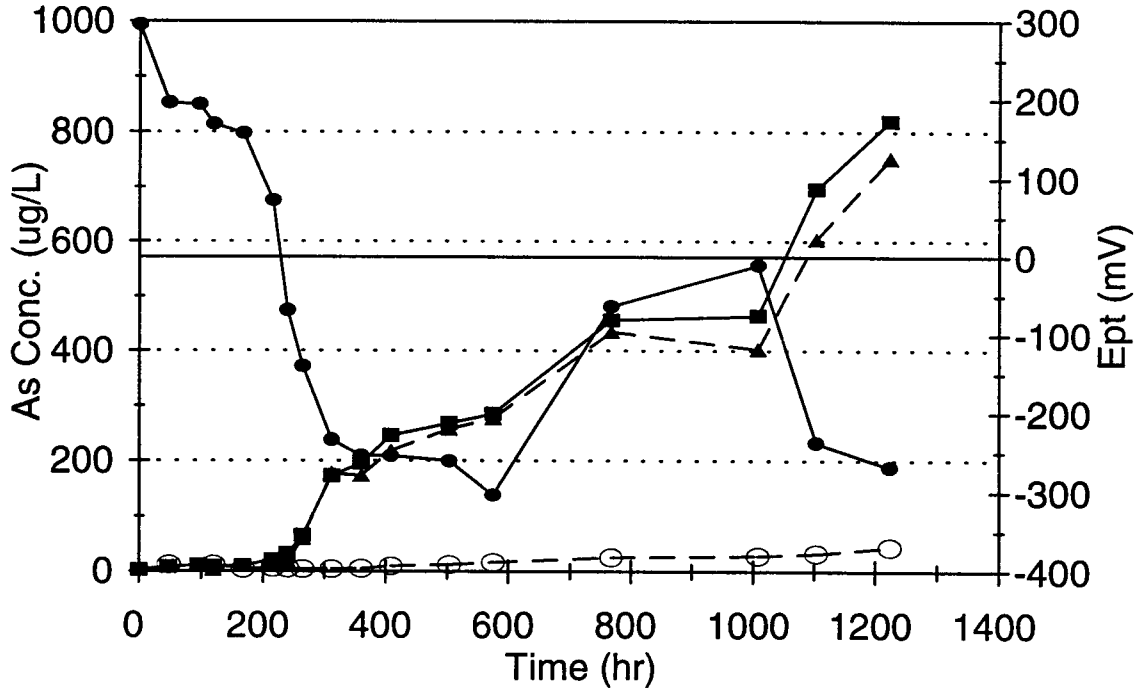


Figure 2.19 Arsenic speciation with time in the arsenic tailings /Bashaw soil slurry experiment (tailing to soil ratio of 3 to 1). Total As measured (■), As(III) (▲), As(V) (○), and E_{Pt} (●).

constant volume in the reactor is not shown in the figure. Total arsenic increased as E_{Pt} decreased as a result of the reduction of As(V) to the more soluble As(III). Significant amounts of As(III) (>50 μg/L) were detected when E_{Pt} was around -100 mV. This behavior is similar to that observed in the controlled reactor study where As(III) was detected in solution in the E_{Pt} range of 0 to -100 mV. The pH of the reactor solution ranged from 7.9 to 8.3 during the course of the experiment.

At the Sutter Creek site, arsenic is assumed to occur mainly as the mineral arsenopyrite (FeAsS) (49), for which the oxidation states of Fe, As, and S are believed to be +2, 0, and -2, respectively (56). In aqueous solution under mildly oxidizing conditions, this mineral and other sulfidic minerals can undergo oxidative dissolution thereby "freeing" the arsenic (57). The oxidation of this mineral is thermodynamically favorable at E_H values above -300 mV at pH 7 (see Appendix B). During or after dissolution, the elemental arsenic can be oxidized to either As(III) or As(V), which can subsequently be removed from solution by adsorption or coprecipitation with Fe oxides.

Arsenate was detected over the entire course of the experiment as a result of the dissolution of iron phases followed by subsequent release of the As(V). Seacor found that the iron content was very high in hydroxylamine hydrochloride extractions (typically 5000 mg/kg) suggesting an association between As and Fe in tailing soil samples (48).

Around 600 hr, E_{Pt} started to increase as a result of O_2 exposure due to depletion of the N_2. However, the total As concentration increased until about 800 hr at which time it began to level off. A fresh tank of N_2 was installed and at about 1000 hr, E_{Pt} decreased and total As began to increase again. The final concentration of 800 μg/L As in solution represented solubilization of only 2% of the arsenic in the tailing soil.

2.4 Conclusions

Determination of arsenic by GFAAS worked well with an AA spectrophotometer equipped with an automatic injection unit and an EDL source. The recommended Ni matrix modifier for samples increased arsenic signals significantly. The required amount of Ni modifier is rather flexible, but optimization of its concentration is recommended. Palladium has been shown to be an effective matrix modifier, yielding arsenic signals almost 50% greater than those obtained with Ni (28). However, Ni remains the more cost effective reagent.

Separate calibration curves are needed for the accurate determination of the concentration of both the As(III) and As(V) species. If one curve was used for both species, significant errors would result. For example, at the 100 µg/L level, the concentration reading of As(V) determined with an As(III) standard curve would be 10% low.

The recommended method for separation of arsenic species by anion-exchange (14) did not work as expected. Acidification of samples with HCl and use of HCl as an eluent for As(III) led to both breakthrough of the As(V) species and suppression of As(III) signals. The protocol was adjusted to include a more extensive resin preparation procedure. A cleaning step with alternate 10-mL washes of 1 M HCl and 1 M NH_4OH was implemented and larger volumes of the conditioning solutions were used to convert the resin into the proper form. Possibly, use of NH_4OH, as opposed to NaOH, also had an effect on the conditioning of the resin.

The suppression of the As(III) signals by HCl was circumvented by use of DI H_2O to elute As(III) into the second fraction. This successfully removed As(III) from the column before elution of the As(V) with HCl. However, the discovery of the suppression effect enabled either concentrated HCl or a mixture of concentrated HCl and HAc to be used as in a qualitative test for the presence of As(III).

The ion-exchange technique with the Dowex anion resin worked well in speciation studies. The resin has sufficient capacity to handle the anions such as NO_3^- and Cl^- that compete with $H_2AsO_4^-$ and $HAsO_4^{2-}$ for sites on the resin. A more stream-lined version of the resin is the recently available anion-extraction disks. To our knowledge, no previous reference has been made to the use of these disks for separation of arsenic species. The main advantage of the disk method is that fewer fractions need to be collected thus decreasing sample processing time compared to the resin technique. The disks are also somewhat easier to use. The disk method worked well for separation of arsenic species as long as the background concentration of competing anions such as Cl^- and NO_3^- was not too high (less than 10 mM). The disk method should work for separation of arsenic species in most surface and groundwaters where typical levels of these two anions are less than 1 mM. Unfortunately, the disk method requires that the pH of samples be adjusted to 7 - 8 to prevent the breakthrough of As(V).

In the original resin technique (14), gravity flow was used. Here, both pumping and gravity flow were tested but both methods were very time consuming. The refined resin technique involved the use of a vacuum manifold in conjunction with small poylpropylene columns packed with the resin. Both refinements greatly increased the number of samples that could be processed while significantly decreasing the time required for processing

each sample. With the vacuum manifold used, up to four samples could be processed in as little as 10 min.

The resin technique was used effectively in the determination of arsenic speciation when either As(III) or As(V) was combined with various redox-active substances (e.g., O_2, MnO_2, Fe(II), Fe(III)). Birnessite (δ-MnO_2), O_2, and H_2O_2 oxidized As(III) to some extent. The extent of the oxidation of As(III) with time by O_2 in aqueous solution has been disputed (32). In this study, the oxidation of As(III) by O_2 ranged from 5 to 40% depending on sample container.

The extent of reduction of As(V) to As(III) was greatest in solutions containing Fe(II). However, reduction of As(V) by Fe(II) was not observed in cases where As(V) was combined with another reagent (e.g., ascorbic acid) before the addition of Fe(II). Arsenate was adsorbed to some extent in all solutions containing Fe(II) or Fe(III). Iron hydroxides are known to adsorb As(V) (35).

The redox behavior of arsenic was studied in a soil suspension in a mini-reactor. Approximately 30% of the arsenate was reduced to arsenite within 24 hr upon injection into a reduced soil environment and the rest was adsorbed. Exposing the solution in the reactor to oxygen resulted in an increase in E_{Pt} followed by a significant decrease in total soluble arsenic, with As(III) being the only detectable species in solution. This type of behavior explains why a popular technique for temporary remediation of contaminated arsenic sites is to till the soil and expose it to oxygen thus keeping the arsenic adsorbed as the As(V) species (55).

The resin technique was also used successfully to monitor the redox behavior of arsenic in the controlled reactor study. In general, as E_{Pt} decreased, total soluble arsenic

and As(III) concentrations increased as As(V) was reduced to As(III) by biotic or abiotic processes. Between 100 and 150 hr, As(III) was initially detected in solution and the indicator started to be reduced as evidenced by a decrease in the absorbance of the oxidized form. In this time frame, the Fe(II) concentration was about 0.3 mM and E_{Pt} ranged from 0 to -100 mV. By the time the indicator was 90% reduced, the As(III) concentration had increased by a factor of 4. Based upon this, it appears that immobilized thionine could be used in a qualitative manner to help predict which form of As will be predominant.

The arsenic concentration measured in creek water from Sutter Creek, Ca. (8 μg/L) was below the maximum contaminant (MCL) for arsenic in water supplies. Arsenate was the only species detected. However, when a sample was preserved with ascorbic acid, a change in speciation occurred and As(III) was the only species detected. The preservation of aqueous samples containing arsenic is tricky in that there are several recommended methods but not everybody agrees on which one is the best. The use of ascorbic acid is one of the simplest but its use here led to erroneous results. The greatest appeal of the ion-exchange technique is that it can be used for in-field separation which eliminates the need for sample preservation.

The tailing material around the Sutter Creek site is enriched with arsenic by a factor of 45 relative to a background soil sample (48). Exposing a sample of the tailing soil to flooded conditions resulted in a significant release of arsenic, as As(III), into solution. When conditions became reducing (E_{Pt} between -100 and -300 mV), up to 800 μg/L soluble arsenic was detected with As(III) accounting for almost 90% of total soluble arsenic. Measurements of the Fe(II) and Mn(II) concentration in solution were not made

during the experiment but could have proven useful. Appearance of either Mn of Fe in solution could be correlated with the appearance of As in solution and could thereby provide insight into which phase of the tailing soil is binding As. Further experiments could be conducted in this area. Also, an extensive mineralogical investigation of As-bearing soil components (i.e., arsenopyrite) present at the site could prove useful.

The final total arsenic concentration in the reduced soil slurry of over 800 μg/L (greater than 700 μg/L As(III)) might be of concern in terms of environmental impact. This arsenic concentration is more than 14 times the MCL for drinking water supplies. However, this As concentration will be affected by environmental factors such as soil to water ratios, contact times, and seasonal redox changes. For instance, the ratio of soil to water in the study was 0.05 (kg soil/L water) and the contact time between the soil and water was about 1200 hr. In the natural setting, the soil to water ratio would be higher and the redox conditions and contact time would vary according to season. However, the potential for the mobilization of As has been shown to exist under natural conditions. Exposure of the tailings in the Sutter Creek area to flooded conditions, as above, could mobilize significant quantities of As.

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Chapter 3
Investigation of Zinc Amalgam as a Reductant

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3.1 Introduction and Historical

Oxidation and reduction reactions are generally described in terms of electron transfer from one reactant species to another. A reactant that shows a strong affinity for electrons is called an oxidant or oxidizing agent; whereas, a reactant that readily donates electrons is termed a reductant or reducing agent. In other words, an oxidant is the species which gains electrons and is reduced while a reductant is the species that loses electrons and is oxidized. The reduction half-reaction is written as follows:

$$ox_1 + ne^- \rightarrow red_1 \tag{3.1}$$

The reduction half reaction is coupled with an oxidation half-reaction:

$$red_2 \rightarrow ox_2 + ne^- \tag{3.2}$$

Equations 3.1 and 3.2 can be combined to yield an overall redox reaction:

$$red_2 + ox_1 \rightleftharpoons ox_2 + red_1 \tag{3.3}$$

A potential E is associated with every half-reaction. When half-reactions are written as reductions, this potential can be described by the Nernst equation as follows:

$$E = E^o - \frac{RT}{nF}\ln\frac{a_{red}}{a_{ox}} \tag{3.4}$$

where E^o is the standard reduction potential (V) defined as the potential where all reactants and products exist at unit activity, R is the gas constant (8.314 J/mol K), T is temperature (K), n is the number of electrons involved in the half-reaction, F is the Faraday (96,485 C), and a represents the activity of the oxidized and reduced species involved in the half-reaction. Often, equation 3.4 is written in terms of concentrations and a formal potential $E^{o'}$ replaces E^o. This latter form can be used in complex situations

where activity coefficients are not known and competing equilibria are significant (4). Formal potentials can also be pH dependent.

Certain analyses require prior oxidation or reduction to aid in the determination of the analyte. In so doing, certain guidelines are important (1):

1) the oxidation/reduction should be rapid,
2) the equilibrium conditions required for a quantitative reaction need to be known, and
3) the presence of excess oxidant or reductant must be handled appropriately.

Applying these guidelines to the use of reductants, one desires a reductant which is powerful enough to reduce many substrates quickly and whose corresponding oxidized form does not interfere in the analysis (i.e., acts as a second reducing agent). For instance dithionite is oxidized to sulfite (15) which itself is a relatively powerful reductant. Common reductants include Sn(II), Cr(II), Fe(II), Ti(III) citrate, dithionite, and metallic reducing agents such as lead or zinc amalgams (1,2,3). Zinc amalgam and dithionite are two of the more powerful reductants based on standard reduction potentials (4,5,14):

Half-reaction	*E^{o} (V)*	*$E^{o'}$(V)(pH 7)*
$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	+ 1.057	- 0.182
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+ 0.770	-----
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+ 0.15	-----
$Pb^{2+} + Hg + 2e^- \rightarrow Pb(Hg)$	- 0.120	-----
$Pb^{2+} + 2e^- \rightarrow Pb(s)$	- 0.126	-----
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	- 0.408	-----
Ti(IV) citrate + $e^- \rightarrow$ Ti(III) citrate	-------	- 0.480

$Zn^{2+} + 2e^- \rightarrow Zn(s)$	- 0.763	-----
$Zn^{2+} + Hg + 2e^- \rightarrow Zn(Hg)$	- 0.762	-----
$SO_4^{2-} + 2e^- + H_2O \rightarrow SO_3^{2-} + 2OH^-$	- 0.936	-----
$SO_3^{2-} + 2H_2O + 2e^- \rightarrow S_2O_4^{2-} + 4OH^-$	- 1.12	-----

Ferrous iron only becomes a moderate reductant at pH values near neutral or above.

When using the homogenous reductants, such as Fe(II), Sn(II), Cr(II), and dithionite, one must be aware of the presence and removal of excess reductant. In the titrimetric determination of iron, Fe(III) is reduced by Sn(II) chloride. The excess Sn(II) must be destroyed by addition of an excess of Hg(II) chloride (1). With the metallic reductants, the reductant is easily separated from the solution by using a packed column of the reductant. Jones (6) is generally credited with initially using amalgamated zinc packed in a column. A column packed with zinc amalgam has since become known as a Jones Reductor.

Zinc is a relatively non-selective reducing agent based on its strongly-negative reducing potential (1). Common metal species reduced include: Fe(III)→Fe(II); V(V)→V(II); Cr(III)→Cr(II); Ti(IV)→Ti(III). The Jones Reductor has been commonly used in determination of iron (2). Fe(III) is reduced to Fe(II), the concentration of which is determined by permaganate titration. Reduction by zinc has found use in hydride generation techniques (12) and in flow-injection analysis techniques (13).

In a study of zinc amalgams, Stone and Hume (7) found the efficiency of reduction was dependent on the amalgamation level and the oxidant. Lighter levels of amalgamation typically resulted in a quicker and more complete reduction. With regards to the nature of the oxidant, they found $CrCl_3$ was reduced more completely than $Cr_2(SO_4)_3$.

The zinc reductor is capable of reducing water or hydrogen ion and thus liberating hydrogen,

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3.5)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (3.6)$$

or reducing oxygen to hydroxide or hydrogen peroxide:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (3.7)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3.8)$$

Burdick (8) found peroxide only when solutions were not acidified. However, Sill and Peterson (9) found hydrogen peroxide was formed in the presence of dilute acid when air was bubbled through the solution and column, with greater amounts being formed by more heavily amalgamated zinc. Lundell and Knowles (10) showed that peroxide was reduced in acid solution when passed through a Jones Reductor.

In general, reduction with zinc amalgam is usually performed in acid solution in order to prevent the formation of hydrogen peroxide, which is potential interferant (3). Hydrogen peroxide in solution can re-oxidize the reduced species in that solution. Use of nitric acid or nitrates is also not recommended because reduction to hydroxylamine and other compounds is possible (2).

A redox indicator is a substance that can undergo oxidation and reduction and exhibit different colors in its two states. Specifically, redox indicators are compounds that react with one form of a redox couple thus causing a visible color change of the indicator. The general half-reaction is:

$$In_{ox} + ne^- \rightarrow In_{red} \quad (3.9)$$

In his book, Bishop (11) has compiled an extensive overview of indicators and their

properties. Indicators are classified in two groups, those with formal potentials less than or greater than the Fe(II)-Fe(III) couple (+0.76 V). No literature references were found pertaining to the use of amalgamated zinc to produce reduced forms of redox indicators.

Presented here is an investigation of zinc amalgam as a reducing agent in the reduction of Cr(III) and selected redox indicators. Studies were conducted with zinc amalgam in a column, the classic Jones Reductor, and in a batch mode. Also, the reduction capabilities of Ti(III) citrate and zinc amalgam were compared.

3.2 Experimental

All absorption measurements were performed with a Hewlett-Packard 8452A diode array spectrophotometer. Reduction of Cr(III) and redox indicators with zinc amalgam was conducted in both batch and column experiments. Batch experiments were performed in a UV/Vis sample cell (Spectrocell, 1-cm pathlength) or 4-mL borosilicate glass vials (Fisher Scientific). Both cell and vial were equipped with septum caps to allow purging and injection of reagents with gastight syringes (Hamilton). Column experiments involved packing a column (Amicon 6.25 in x 0.5 in i.d.) with amalgamated zinc. The column was packed up to about the 5 in mark leaving space to observe the level of liquid above the bed.

The zinc was amalgamated as follows.

1) The appropriate amount of zinc (Mallinckrodt, Zinc Metal AR, 20 mesh (595 to 841 μm)), typically 20 to 30 g with the Amicon column, is weighed out and placed in a small Erlenmeyer flask.
2) A solution of 0.1 - 2% (w/v) $HgCl_2$ is made by dissolving the appropriate amount of $HgCl_2$ (Mallinckrodt), 0.1 - 2 g/100 mL, in DI H_2O.
3) The $HgCl_2$ solution is then added to the Erlenmeyer flask until the zinc is covered.
4) A few drops of concentrated HCl (Mallinckrodt) are then added to the flask and the contents are stirred for 5 - 10 min.

After stirring, the amalgamated zinc is ready for use. The zinc is classified as 0.1 - 2% amalgamated depending upon the concentration of the $HgCl_2$ solution used. In the

literature, the amalgamation levels are not always clearly defined. Here, the definition is operational and does not imply a specific Hg/Zn mass ratio.

Initial experiments involved reducing Cr(III). Originally, Cr(III) solutions were made from $Cr(NO_3)_3$, but because nitrates lead to interferences (2), it was decided that $CrCl_3$ should be used. A 1000 mg/L solution of $CrCl_3$ was made by dissolving 0.5126 g of $CrCl_3 \cdot 6H_2O$ (Mallinckrodt) in 500 mL of DI H_2O. The solution was then adjusted to pH 3 with concentrated HCl followed by dilution to 1000 mL. This stock solution was used to prepare the various Cr(III) solutions needed.

The list of redox indicators used in reduction experiments appears in Table 3.1 along with formal potentials at pH 7 and the vendor. Solutions with the concentrations specified in Table 3.1 were made by dissolving the appropriate amount of indicator in 100 mL of DI H_2O. The pH of the solutions were typically between 3 - 4.

3.2.1 Batch Reduction of Cr(III) and Redox Indicators

To begin batch reduction experiments, approximately 1 g of freshly prepared 2% amalgamated zinc was placed in the sample cell. Next 3.5 mL of a N_2 deaerated solution of 0.01 M $CrCl_3$ at pH 3 were added to the cell. The cell was then placed in the spectrophotometer and scanned from 300 to 820 nm. The cell headspace was continually purged with N_2 during scanning. For all purging operations throughout this work, N_2 was introduced via a syringe needle connected to 1/8 in o.d. Teflon tubing with a 1/4 - 28 in luer tip converter. The Teflon tubing was connected to the regulator of the N_2 tank. The N_2 was analytical grade and was not "scrubbed" to remove contaminant O_2.

Table 3.1 Indicators used in Reduction Study

Indicator	Conc. Used (μM)	$E^{o'}$ (pH 7) (V vs SHE)	Vendor
Brilliant Cresyl Blue	20	0.047	Sigma
2,6-Dichloroindophenol (DCIP)	50	0.224	Baker
Indigo Carmine	20	- 0.125	Aldrich
Indigo Tetrasulfonic Acid (ITESA)	20	- 0.046	Aldrich
Methylene Blue	20	0.011	Aldrich
Napthol Blue-Black	20	------	Sigma
Neutral Red	50	- 0.325	Aldrich
Nile Blue	20	- 0.119	Aldrich
Phenosafranine	20	- 0.252	Aldrich
Safranine O	20	- 0.289	Aldrich
Thionine	20	0.064	Aldrich
Varamine Blue	120	0.310	Sigma

Solutions were made slightly acidic, in addition to purging, to prevent possible formation of peroxides and hydroxides from reduction of residual O_2.

Because results of initial experiments indicated no significant dependence of the efficiency of reduction on the level of amalgamation, most remaining experiments were performed at the 0.1% amalgamation level. Stone and Hume found that higher amalgamation levels resulted in less efficient reduction of $CrCl_3$ (7).

For batch experiments with redox indicators, 3.5 mL of the indicator was placed (pH 3 - 4) in a 4-mL borosilicate glass vial. The solution was then deaerated for 3 - 5 min with N_2. Next 1.0 - 1.5 g of 0.1% amalgamated zinc was then added to the vial and the vial was immediately recapped and the headspace was purged with N_2. The color of solutions at zero and 48 hr was recorded. After 48 hr, the vials were opened and exposed to air for another 48 hr. Spectrophotometric analysis of indicators in batch-type experiments was not performed.

3.2.2 Column Reduction of Cr(III) and Redox Indicators

The apparatus used in column reduction experiments is illustrated in Figure 3.1. All tubing was Teflon with 1/8 in o.d. A syringe needle was connected to the other end of the outlet tubing for transfer into sample cells. The solution to be reduced was placed in a filter flask with a N_2 balloon attached and then deaerated with N_2 for 3 - 5 min. The solution was then pumped (Fluid Metering Inc. Micro-Pipetter) to a three-way valve (Rheodyne Model 5301) where solution could be directed to the column or removed for

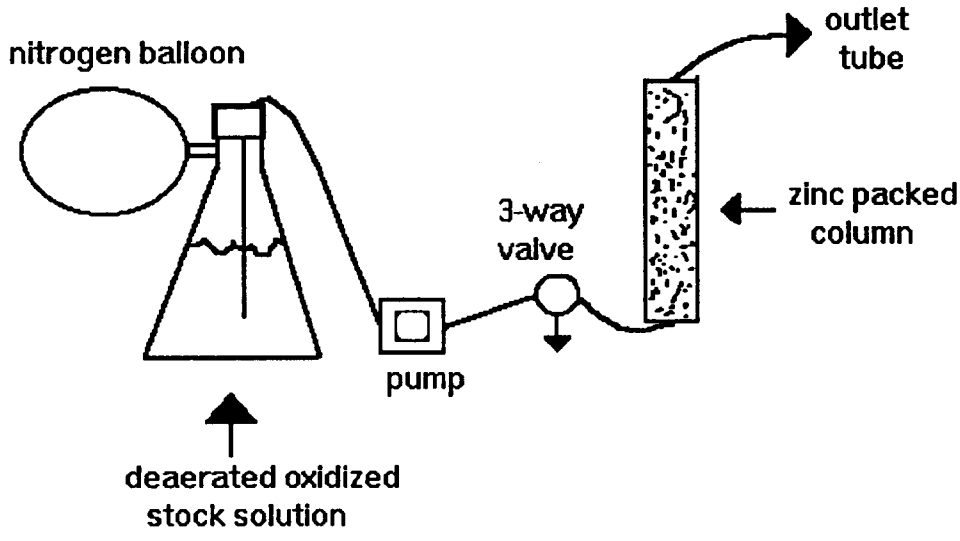


Figure 3.1 Reduction column apparatus.

pre-column analysis. Solutions were directly collected in the sample cell, placed in the spectrophotometer and scanned from 300 to 820 nm.

The procedure used for column reduction of Cr(III) and the indicators is detailed below.

1) Amalgamated zinc was placed in column (Amicon 6.25 in x 0.5 in i.d.) and rinsed sequentially with 0.1 M HCl for 3 min and DI H_2O for 5 min at a flow rate of 5 - 7 mL/min.
2) The system (lines, column, pump) was flushed with N_2 by running the pump with the empty flask under N_2 pressure.
3) The solution to be reduced was placed in the filter flask and deaerated for 3 -5 min after which the N_2 balloon was allowed to fill.
4) Sample was then pumped at a flow rate of 1.5 - 2.0 mL/min through the system.
5) Sample was removed, before it entered the column, at the three-way valve and a pre-column scan was performed.
6) The valve position was then switched such that solution was directed through the column. After 12 - 13 min, the needle attached to the column outlet tubing was inserted though the septum of the sample cell, which had been purged with N_2, and the column effluent was collected. After collection of 2 - 3 mL of effluent, a post-column scan was performed.

Any dilution of a given test solution, due to entrapment of the previous solution in the column, was corrected by the wait period of 12 -13 min. The flow of solution was directed up the column as opposed to down the column because preliminary studies demonstrated that this flow direction improved efficiency of reduction and consistency of

results. Pumping was used as opposed to gravity flow because it provided better control of flow rate. Reducing the flow rate to less than 1.5 - 2.0 mL/min did not appear to improve the reduction efficiency of the column. Use of faster flow rates generally resulted in a decrease in the reduction efficiency of the column.

Smaller columns (e.g., 5 cm x 5 mm i.d.) were tried in the reduction of Cr(III). The extent of reduction of Cr(III) was similar between these columns and the Amicon column, but the Amicon column was easier to use. In addition, the use of the Amicon column led to a greater extent of reduction for the indicators as a result of the larger bed volume and subsequent longer contact time. Also, instead of keeping the column filled with solution between runs to prevent contact of the Zn with air as has been recommended (2), the column was simply purged with N_2 and kept under N_2 pressure with the aid of the N_2 balloon on the side-arm flask.

The zinc reduction column was used for typically 1 - 2 weeks before reduction efficiency decreased. For storage, the column was washed sequentially with 0.1 M HCl and DI H_2O and then flushed with N_2. Next the column was capped to prevent contact with air. After the zinc reductor column had lost its effectiveness, as evidenced by a decrease in the reduction efficiency, "recycling" of the zinc was attempted by washing it several times with 1 M HCl followed by amalgamating as described previously.

3.2.3 Reduction Studies with Titanium Citrate

The homogenous reducing agent Ti(III) citrate and metallic zinc amalgam were compared on the basis of their ability to reduce reversibly the redox indicator thionine.

Here, reversibly reduce means that the reduced indicator can be converted back to its fully oxidized form. The procedure for preparation of the solution of Ti(III) citrate is a modification of a literature procedure (14) and is given below.

1) About 8 g of Tris buffer (Enzyme grade, BRL Life Technologies Inc.) and 14.7 g of sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, Mallinckrodt) were added to about 40 mL of DI H_2O in a 150-mL beaker, and stirred until contents were dissolved. The beaker was capped with paraffin and purged with N_2 continually.
2) Approximately 30 mL of $TiCl_3$ (Fluka Chemika) were then added to the beaker with continuous purging.
3) The solution was then placed in an ice bath and the pH is adjusted to 7 using NaOH pellets (Mallinckrodt) with continuous stirring and purging.
4) The solution was next transferred to a 100-mL volumetric flask and the solution was brought up to 100 mL total volume. The Ti(III) citrate concentration was approximately 240 mM.
5) The solution was placed in several 8-mL borosilicate glass vials (Fisher Scientific) equipped with septum caps (Alltech). Each vial was then purged with N_2 for a few minutes and stored in the freezer.

Reduction of thionine with Ti(III) citrate and and re-oxidation with H_2O_2 was done as follows.

1) Exactly 4 mL DI H_2O was placed in the sample cell and purged with N_2 for 3 - 5 min after which a blank scan from 300 to 820 nm was performed.
2) Next, 60 μL of 2 mM thionine was injected into the cell and the absorbances at 600 and 820 nm were recorded.

3) Then, 5 μL of 240 mM Ti(III) citrate was injected and the absorbances at 600 and 820 nm were monitored until they stabilized.

4) Next, 100 μL of 0.1 M H_2O_2 was added and the absorbances at 600 and 820 nm were again monitored and allowed to stabilize as above.

Reduction of thionine with the Jones Reductor was performed as described in the section on column reduction. Approximately 3.5 mL of reduced thionine was collected in the sample cell and re-oxidation was performed by injecting 58 μL of 0.1 M H_2O_2 which resulted in the same excess of peroxide that was present at the end of the reduction/re-oxidation experiment with Ti(III) citrate. Even with excess peroxide, thionine could not be fully re-oxidized after reduction by Ti(III) citrate.

In an attempt to increase the extent of re-oxidation, experiments were performed in 1 M citrate buffer with the goal of keeping the Ti(IV) complexed with citrate to prevent its precipitation. A 1 M citrate buffer was made by dissolving 11.5 g of $H_3C_6H_5O_7 \cdot H_2O$ (Mallinckrodt) and 14.5 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ (Mallinckrodt) in 100 mL of DI H_2O. The pH of the buffer was then adjusted to 4. Exactly, 3.5 mL of 1 M citrate buffer was placed in the cell and the experiment was performed as noted above.

3.3 Results and Discussion

3.3.1 Batch Reductions

Zinc amalgam was used both in batch and column experiments to produce reduced forms of Cr(III) and various redox indicators. Figure 3.2 shows spectra that confirm the batch reduction of $CrCl_3$ by zinc amalgam. Successful reduction required solutions to be slightly acidic (pH 2-4) and deaerated with N_2 prior to reduction. Initial stock solutions of Cr(III) were made from $Cr(NO_3)_3$. Because only slight reduction of $Cr(NO_3)_3$ solutions was observed and nitrates have been shown to cause interferences (2), stock solutions were subsequently made from $CrCl_3$. Experiments comparing amalgamation levels (0.1 - 2%) proved inconclusive, and after examination of the literature (7), a level of 0.1% was used for the majority of the experiments.

Table 3.2 lists the results of batch reduction of selected redox indicators evaluated in this study. Although a few indicators appeared to be marginally reduced by zinc amalgam, the majority appeared fully reduced based upon the absence of color in solution. However, upon increasing the concentrations of indicators above those listed in Table 3.1, significant reduction of the indicator was not readily observable. For example, reduction of a 1 mM solution of phenosafranine led to the formation of a yellow-brown precipitate instead of a colorless solution. Some of the solutions appeared cloudy after reduction. The cloudiness resulted from the presence of precipitates. These precipitates may have formed by combination of ionic metal species (e.g., Hg^{+}, Hg^{2+}, Zn^{2+}) with hydroxides or other anionic species which may have been present. For column experiments, it has been

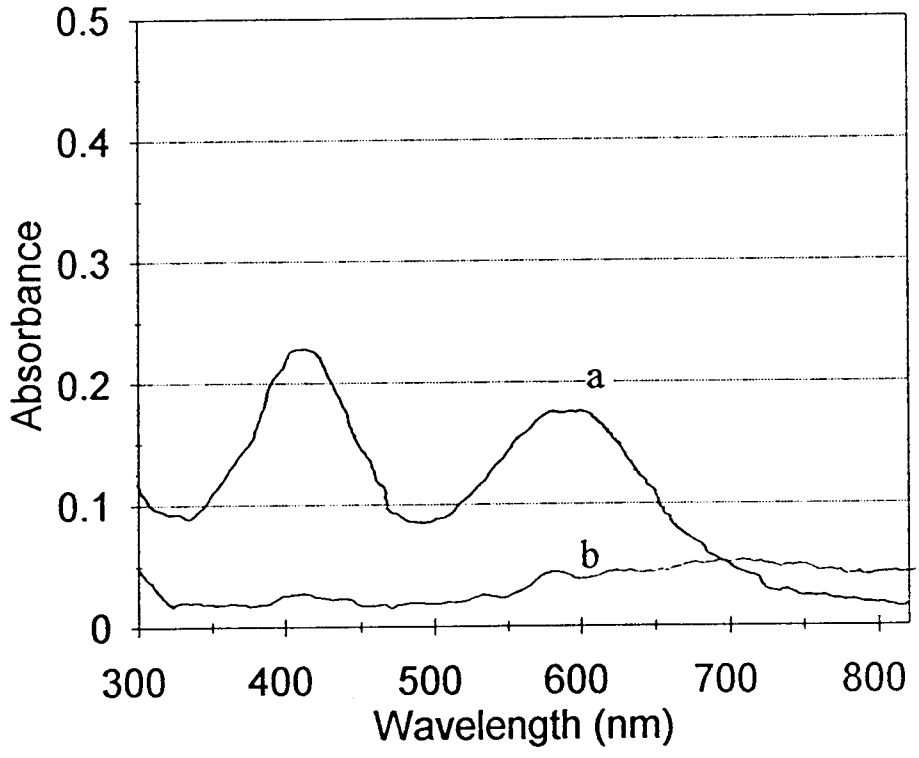


Figure 3.2 Spectra illustrating batch reduction of 0.01 M Cr(III) (pH 3) with zinc amalgam: (a) before addition of zinc amalgam; (b) 1 hr after addition.

Table 3.2 Batch Reductions of Indicators with Amalgamated Zinc[a]

Indicator	Conc. (μM)	Color t = 0 hr	Color t = 48 hr	Color (vial opened)[b] t = 96 hr
Brilliant Cresyl Blue	20	blue	clear, faint cloudiness	blue
DCIP	50	light blue-purple	clear	light blue-purple
Indigo Carmine	20	blue	clear	clear
ITESA	20	light blue	light yellow	clear
Methylene Blue	20	blue	light blue, cloudy	blue with ppt.
Napthol Blue-Black	20	dark blue	clear	gray
Neutral Red	50	orange-pink	clear, faint cloudiness	peach
Nile Blue	20	aqua blue	clear, faint cloudiness	blue
Phenosafranine	20	pink	clear	pink
Safranine O	20	pink	clear	pink
Thionine	20	purple	clear	purple
Varamine Blue	120	gray-blue	clear	gray-red

[a] Performed in 4-mL sample vials with an amalgamation level of 0.1%.
[b] After t = 48 hr, the vials were opened and exposed to the air for another 48 hr.

recommended (2) that the column of zinc be kept full of water in order to prevent contact with air which may result in the formation of basic salts which clog the column.

3.3.2 Column Reduction

The efficiency of the column reductor was evaluated quantitatively by the percent reduction which is defined by the following equation:

$$\% \ reduction \ = \ \frac{(A_c)_{pre} - (A_c)_{post}}{(A_c)_{pre}} \ x \ 100 \qquad (3.10)$$

where $(A_c)_{pre}$ is the pre-column corrected absorbance of the indicator and $(A_c)_{post}$ is the post-column corrected absorbance. A background absorbance is taken at 820 nm for both pre- and post-column scans to compensate for spectrophotometer source drift. This background absorbance is then subtracted form the absorbance at the analytical wavelength (the wavelength of maximum absorption of the visible absorption band of the oxidized form) to give a corrected absorbance A_c. For example, for thionine, A_c is calculated as follows:

$$A_c \ = \ A_{600} \ - \ A_{820} \qquad (3.9)$$

Figure 3.3 shows spectra that confirm the reduction of Cr(III) with the reductor column. Both techniques gave 95 - 100% reduction of Cr(III).

Column reduction of Cr(III) with "recycled" amalgamated zinc which had lost its effectiveness and had been acid washed and re-amalgamated was partially successful.

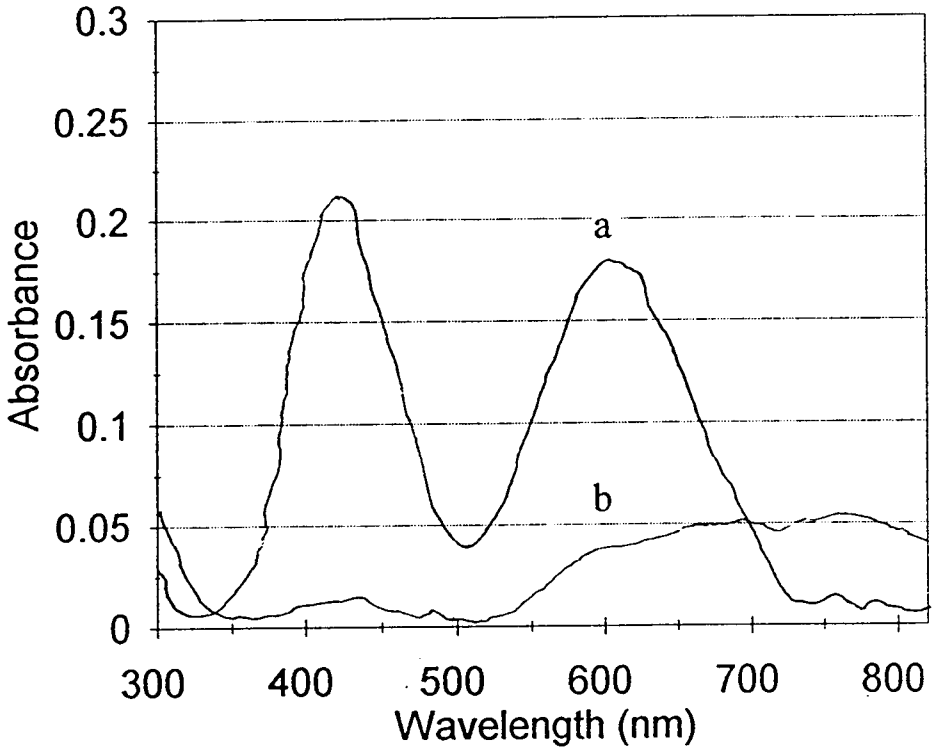


Figure 3.3 Spectra illustrating reduction of 0.01 M Cr(III) (pH 3) with the Jones Reductor: (a) pre-column analysis; (b) post-column analysis.

The spectra in Figure 3.4 shows that the efficiency of reduction of Cr(III) is over 30% better with "fresh" zinc relative to "recycled" zinc.

The conditions and results for reduction of redox indicators, with Zn amalgam in the column format, are given in Table 3.3. Figure 3.5 shows oxidized/reduced spectra for selected redox indicators. The reduction efficiency for the indicators ranged from 15 - 100%. The reductor column was not as effective as the batch reductor at reducing certain indicators. For example, in batch-type experiments, indigo carmine appeared fully reduced, while in column experiments, only 14% reduction could be obtained. This difference is attributed to longer contact time between the indicator and the zinc amalgam in batch studies. Typical contact times in batch experiments were 24 hr or more; whereas in column experiments, contact times were approximately 10 min or less based on the column void volume (~ 9 mL) and flow rate (1 to 2 mL/min). Attempts at re-circulating solutions of the harder-to-reduce indicators back through the column in order to increase contact times, did not significantly increase the percent reduced.

3.3.3 Reduction with Ti(III) Citrate

Both the Jones Reductor and Ti(III) citrate efficiently reduced the redox indicator thionine as illustrated by the spectra in Figure 3.6. Figure 3.6 also illustrates that the extent of re-oxidation of thionine with hydrogen peroxide is less in solutions reduced with Ti(III) citrate than in solutions reduced by the zinc reductor (82% vs. 95%). In the case of Ti(III) citrate, the Ti(III) is converted to Ti(IV), which may form insoluble hydroxide precipitates which absorb thionine. This hypothesis was supported by the results observed

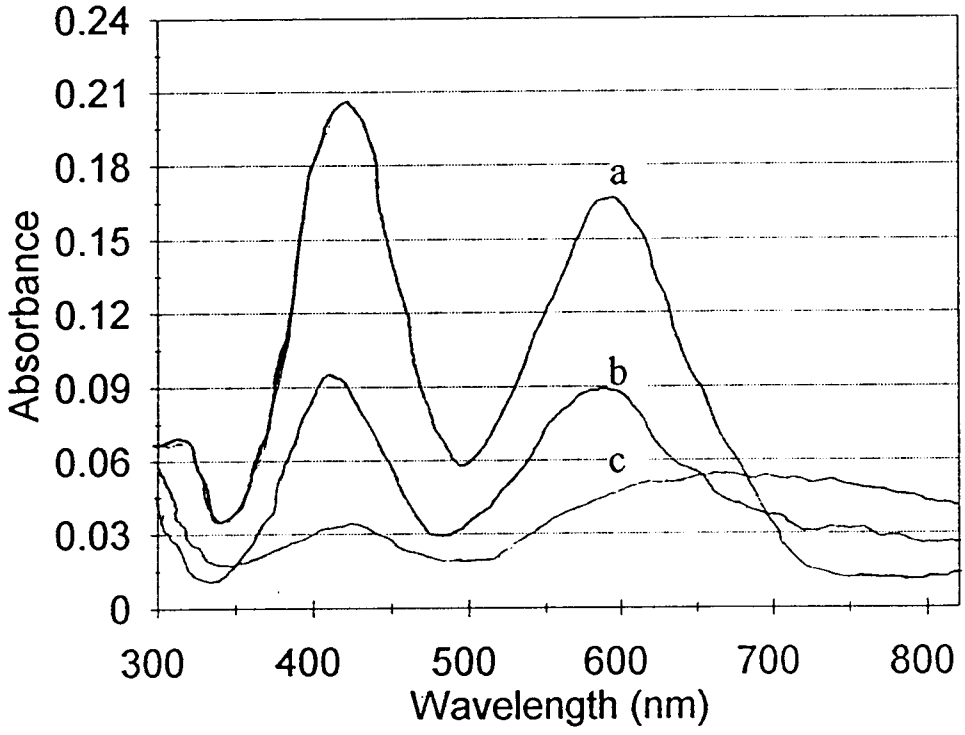


Figure 3.4 Comparison of spectra for reduction of 0.01 M Cr(III) (pH 3) with fresh and recycled zinc in the Jones Reductor: (a) pre-column analysis; (b) recycled; (c) fresh.

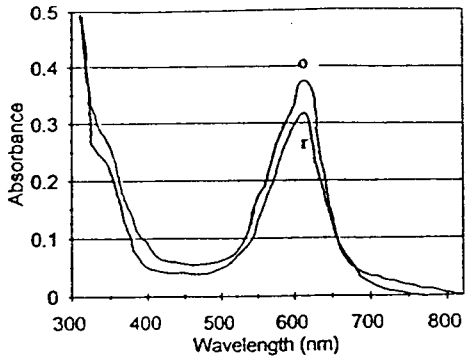
Table 3.3 Reductions of Indicators with the Jones Reductor[a]

Indicator	Conc (μM)	Wavelength (nm)	Pre-Column Color	Post-Column Color	% Reduction (n = 2)[b]
Brilliant Cresyl Blue	20	626	blue	blue	62 (4)
DCIP	50	590	blue	clear	84 (1)
Indigo Carmine	20	610	blue	blue	14 (1)
ITESA	20	590	violet-blue	light purple	76 (3)
Methylene Blue	20	666	blue	light blue	84 (4)
Napthol Blue-Black	20	616	dark blue	light purple-blue	89 (6)
Neutral Red	50	560	red-pink	orange-rust	97 (1)
Nile Blue	20	634	blue	light blue	63 (3)
Phenosafranine	20	520	pink	pink	71 (3)
Safranine O	20	520	pink	pink	35 (1)
Thionine	20	600	blue	clear	93 (3)
Varamine Blue	120	626	gray-blue	light blue	nd[c]

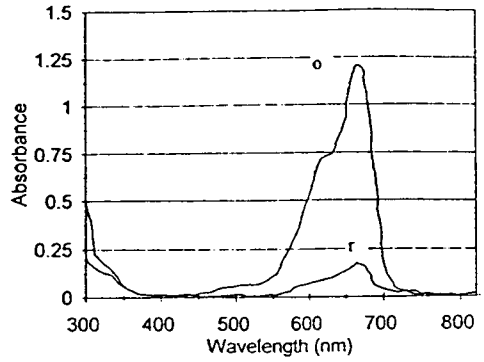
[a] Conditions used: column 6.25 in x 0.5 in i.d.; flow rate = 1.7 mL/min; column rinse (5-6 mL/min) = 3 min 0.1 M HCl, 5 min DI; N_2 flush time = 2 min; solution dearaete time = 3-5 min; post-column sample delay = 12-13 min; amalgamation level = 0.1%.

[b] Experimental standard deviation is shown in parenthesis (n = 2).

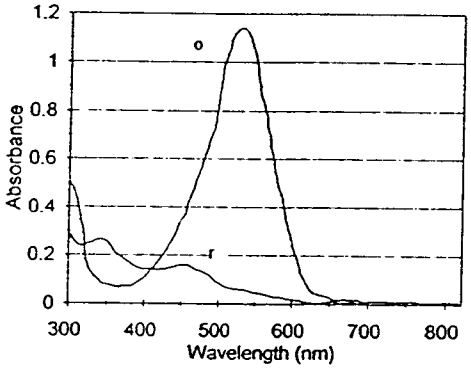
[c] Percent reduction of varamine blue was not determined in this study.



a



b



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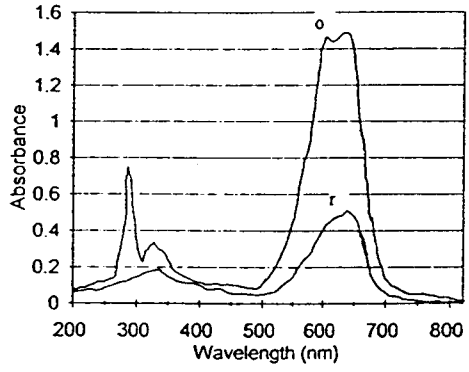

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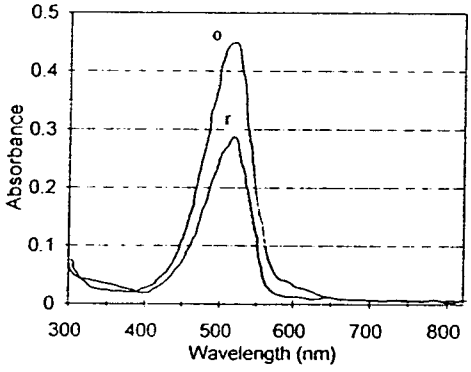

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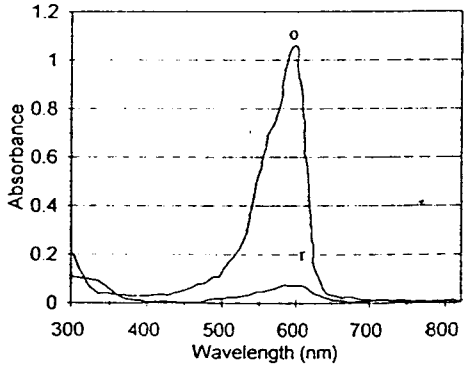
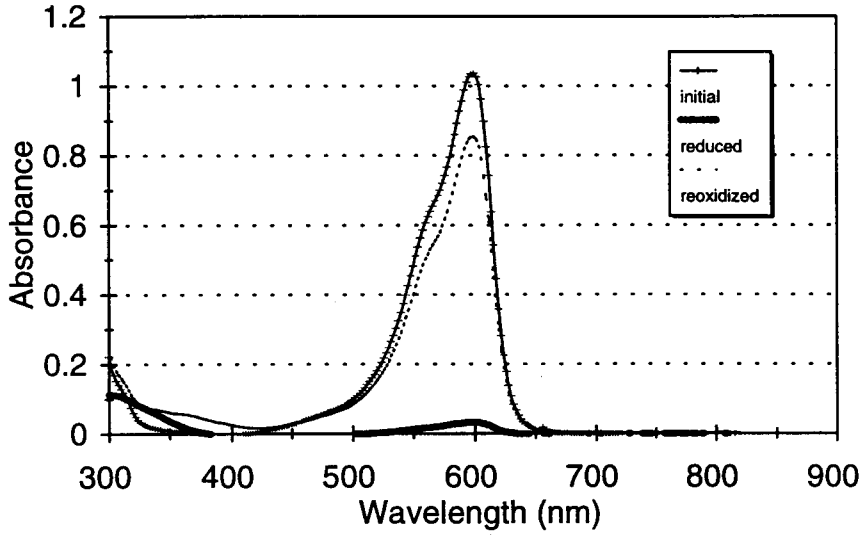
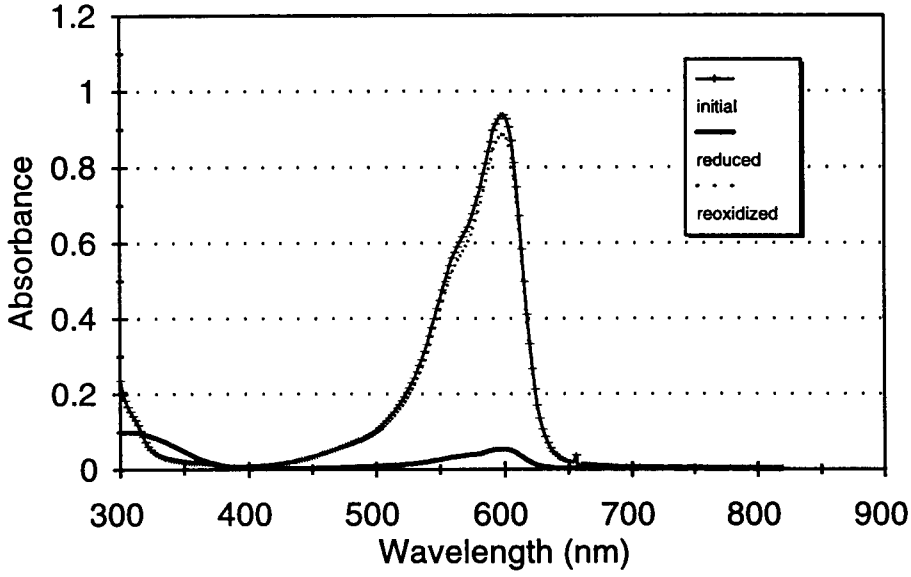


f

Figure 3.5 Spectra illustrating reduction of selected redox indicators with the Jones Reductor: (o) pre-column; (r) post-column. Spectra shown are: (a) indigo carmine; (b) methylene blue; (c) neutral red; (d) nile blue; (e) safranine O; (f) thionine. Indicators at pH 3 - 4.



(a)



(b)

Figure 3.6 Spectra illustrating reduction of thionine followed by re-oxidation with H_2O_2. Thionine reduced with: (a) titanium citrate; (b) Jones Reductor. Re-oxidation is more complete in the Jones Reductor case.

when the experiments were repeated in the presence of excess citrate, which should help keep Ti(IV) complexed and in solution. In the presence of citrate, the oxidation efficiency improved from 82% to 96%. The reason for incomplete oxidation after reduction by zinc amalgam could also be attributed to loss of thionine by adsorption on precipitates formed in the reduction of water by the zinc amalgam. White and gray percipitates were frequently observed in the column after it had set for a day or two without use. These percipitates formed even when the column had been purged with N_2 and capped. An additional consideration of using zinc amalgam as a reducing agent is the amount of Zn^{2+} which is formed in the oxidation reaction.

3.4 Conclusions

Zinc amalgam was used effectively to produce reduced forms of Cr(III) and various redox indicators. In the batch mode, zinc amalgam appeared to reduce quantitatively Cr(III) and most of the redox indicators tested within 24 hr or less. An initial goal of this study was to produce Cr(II) by reduction of Cr(III) and then use the Cr(II) to reduce the indicators. However, the need for Cr(II) was circumvented by using zinc amalgam directly to reduce the indicators. No references have been found pertaining to the use of zinc amalgam to produce reduced forms of redox indicators.

Zinc amalgam in the column mode also reduced Cr(III) and the indicators. The apparatus was simple to assemble and proved easy to use. Near 100% of the Cr(III) was reduced in column experiments. However, the reduction efficiency of the redox indicators in the column experiments ranged from 15 - 100%, and was generally poorer than with the batch mode. The lower reduction efficiency is attributed to the lower contact time between the zinc amalgam and indicator in the column method (~ 10 min) relative to that used for batch experiments. Contact times and thus the extent of reduction of the indicators in column experiments could possibly be improved by using a longer column, very slow flow rates, or a more efficient re-circulation design. Use of smaller particles of zinc may also improve percent reductions. Additional improvements could include O_2 scrubbing of the N_2 used for purging along with the use of tubing which is less O_2 permeable than Teflon.

Both Ti(III) citrate and zinc amalgam effectively reduced the indicator thionine, but upon re-oxidation with hydrogen peroxide, the initial absorbance could not be reached.

This effect was more pronounced for Ti(III) citrate than for the zinc reductor. In the case of Ti(III), it was speculated that thionine was removed from solution by adsorption on Ti(IV) hydroxides formed by the oxidation of Ti(III).

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Chapter 4
Conclusions

Two related techniques for the determination of arsenic speciation have been developed. They are simple and are based upon anion-exchange coupled with graphite furnace atomic absorption spectrophotometry (GFAAS). The first technique is a refinement of a published technique which utilizes a strong anion-exchange resin in a column to separate As(V) from As(III). The second technique utilizes the recently available Empore anion-extraction disks. Conditioning and elution schemes were optimized so that the neutral arsenite is not retained by the resin or disk, while the monovalent or divalent arsenate species is retained and later eluted with 0.1 M HCl.

The published speciation method was refined to include alternate washes with HCl and NH_4OH, which effectively cleaned the disk or resin. A second refinement was to increase the volume of conditioning solutions to obtain a higher degree of conversion of the resin or disk to the acetate form which assures the retention of As(V). The third refinement was the addition of an elution step with H_2O to remove As(III) from resin prior to elution of the As(V) with HCl. Although As(III) is not retained, there is some hold-up in the interstitial volume. It was discovered that As(III) signals were suppressed in the presence of HCl, which had been used for removal of As(III) in the published method.

Percent recoveries of As(III) and As(V) ranged from 94 to 99% with both techniques. The detection limit of 2 μg/L with GFAAS is satisfactory for determination of arsenic speciation in surface waters or groundwaters of contaminated field sites.

The 1 g of resin used provides a greater capacity than that of the 13-mm extraction disk (2 meq vs 0.043 meq) and therefore is capable of handling higher concentrations of background anions, such as Cl^- and NO_3^-, that can interfere with the retention of As(V). However, the extraction disks are suitable for separation of arsenic species in most surface and groundwaters where levels of Cl^- and NO_3^- are typically less than 1 mM. Larger diameter disks or disks in series could potentially improve the applicability of the disks to higher levels of anions. The method also offers a simple method for preconcentration of As(V). By increasing the sample volume, detection limits below 1 µg/L As(V) are obtainable. Detection limits for the separated As species could also be improved with ICP/MS detection. Future studies could be directed at speciation of inorganic arsenicals as well as organic arsenicals through the use of a mixed cation/anion resin bed or a combination cation/anion disk configuration. Grabinski (reference #38, Chap. 2) has shown that organic arsenicals are retained by a cation-exchange resin.

The separation technique was used successfully to monitor the oxidation of As(III) and reduction of As(V) with specific redox-active substances. Hydrogen peroxide, O_2, and δ-MnO_2 oxidized As(III) to As(V) to some extent. Reduction of As(V) to As(III) was most extensive in solutions containing Fe(II). Adsorption of As(V) always occurred to some degree in solutions containing Fe(II) or Fe(III) as evidenced by loss of arsenic from solution.

Arsenic redox behavior was studied in soil slurry mixtures in two reactor systems. Upon injection of As(V), the As(V) was adsorbed extensively and total soluble arsenic was low. When conditions became reducing due to microbial action as indicated by E_{Pt} values below -50 mV, total soluble arsenic increased and As(III) became the predominate

species in solution. When the contents of the reactor were exposed to oxygen or H_2O_2 was added, total soluble arsenic decreased significantly due to oxidation of As(III) followed by adsorption of the As(V).

In the controlled reactor study, the Fe(II) concentration and absorbance of immobilized thionine were monitored along with arsenic speciation. In previous experiments, solutions of Fe(II) reduced the immobilized indicator. In the present study, a change in the indicator absorbance correlated with the appearance of As(III) in solution. It appears that As(V) was reduced under the same conditions as that required for reduction of the indicator and therefore, immobilized thionine could possibly be used qualitatively to predict which form of As will be predominant in solution.

The ion-exchange technique was applied successfully in the field to determine the speciation in creek water at Sutter Creek, Ca. Preservation of samples with ascorbic acid resulted in reduction of soluble As(V) to As(III). This phenomenon pinpoints the problem of sample preservation as is required in the use of speciation techniques such as the hydride generation technique. An improper preservative may lead to a change in arsenic speciation between sample collection and analysis. A major appeal of the ion-exchange technique is that a sample preservative is not required because the separation of arsenic species can be performed immediately in the field before a significant change in speciation can occur.

When mine tailing soil from the Mesa de Oro area was combined with organic-rich Bashaw topsoil followed by removal of O_2 (to simulate flooded conditions), significant amounts of arsenic were released into solution as the As(III) species. If the attempt is made to isolate the As in the tailing soil by placing additional topsoil over the existing

tailing/topsoil mixture, flooding and anoxic conditions could lead to significant amounts of arsenic being leached out of the tailings. This type of behavior should be considered in planning future remediation of the area.

Future studies of arsenic redox behavior in either the Bashaw soil slurry or the tailing soil/Bashaw soil slurry should focus on what mineral phases are important in oxidizing, reducing, or adsorbing As species. For example, a more extensive investigation of the mineral phases (i.e., Mn oxide isomorphs, Fe hydroxide isomorphs) could aid in understanding the mechanism for both adsorption and oxidation of As(III) as well as adsorption and reduction of As(V). The determination of arsenic speciation in soil slurries is difficult in that adsorption or coprecipitation of species must always be considered. The influence of direct or indirect microbially-mediated processes on the speciation of As should also be considered .

Zinc amalgam in both batch and column formats was used to reduce Cr(III) and various redox indicators. In the batch mode, complete reduction of both Cr(III) and redox indicators was achieved over a 48 hr period. Nearly 100% of the Cr(III) was reduced in the zinc column. However, the reduction efficiency of the redox indicators with the column format ranged from 15 - 100% and was generally poorer than with the batch mode. This behavior is attributed to slow reduction kinetics and insufficient contact time between the indicator and reductant. The reduction efficiency of the indicators could possibly be enhanced by using a longer column, very slow flow rates, smaller particles of zinc, or a more efficient re-circulation design.

Both Ti(III) citrate and zinc amalgam effectively reduced the indicator thionine, but upon re-oxidation with H_2O_2, the absorbance measured prior to reduction and re-oxidation

could not be reached. This effect was more pronounced for Ti(III) citrate than for the zinc reductor. In the case of Ti(III), it is speculated that thionine was removed from solution by adsorption on Ti(IV) hydroxides formed by the oxidation of Ti(III).

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Appendices

Appendix A

Environmental Redox Behavior of Arsenic

Arsenite is more toxic, soluble, and mobile than arsenate (6,7,8). In aerobic soils and oxygenated waters, arsenate should dominate arsenite; however, thermodynamic ratios are rarely observed and many factors must be considered in the redox behavior of arsenic. The presence of oxides and other redox active species affects arsenic speciation and solubility. Variables such as the potential at a Pt electrode (E_{Pt}), often termed the redox potential, and pH play a major role in arsenic redox behavior.

Presented here is a brief literature review of the environmental behavior of arsenic. Oxidation/reduction behavior is discussed first. Studies involving the use of synthetically prepared minerals and naturally occurring minerals are reviewed. Topics include potential oxidants or reductants, kinetics, and mechanisms of oxidation/reduction. Next the adsorptive/desorptive behavior of arsenic is discussed. Various adsorbents reviewed include Mn, Fe, Al oxides and clays. The discussion is again divided into synthetic and natural studies. Topics include the adsorptive properties of various minerals, adsorptive capacities, and rates and mechanisms. Finally, biological methylation is briefly discussed. For more extensive details of topics discussed, the reader is referred to the bibliography which follows the appendix.

Oxidation/Reduction

The oxidation/reduction behavior of As is peculiar. For instance, workers found that As(III) was oxidized in solutions of deionized water whereas As(V) was reduced in

solutions of filtered river water (1). In other experiments, As(III) was oxidized in freshwater samples which had been frozen and the concentration ratio of As(III)/As(V) in seawater samples was found to be unstable to freezing unless dry ice was used (1,2). Haswell et al. (3) found that arsenite was oxidized within 5 hours in unfiltered pore waters from mineralized and unmineralized sediments. Feldman (4) reported that near complete oxidation of As(III) at the μg/L level occurred in aqueous solution within 1 week. In contrast, Tallman and Shaikh (5) reported that aqueous solutions containing As(III) and As(V) at μg/L levels could be stored at least 3 weeks without significant conversion between As(III) and As(V).

Dissolved oxygen and Mn(IV) and Fe(III) minerals are capable of oxidizing As(III) to the less toxic As(V) (9,10). Certain organisms can also oxidize As(III) (9). The presence of oxidizing organisms could significantly affect As(III) and As(V) concentrations in solution.

Oscarson et al. (10) have extensively studied the oxidation of arsenic by Mn and Fe oxides. Thermodynamically Mn(IV) and Fe(III) oxide can both act as primary electron acceptors in the oxidation. In studies of the oxidative power of synthetic Mn(IV) (as birnessite) and Fe(III) oxides with respect to As(III), it was found that after addition of 1000 μg/mL As(III) to 100 mg Mn (IV) oxide, 216 μg /mL As(V) was produced corresponding to 19% reduction of Mn(IV) to Mn(II). In control experiments, no measurable oxidation of As(III) occurred in the absence of Mn(IV) oxide. The extent of oxidation was much less in soil samples in which the Mn had been extracted. With increasing concentrations of As(III) above 300 ug/mL, soluble As(V) concentration increased slightly and soluble Mn concentration actually decreased. Apparently the

reduction of Mn(IV) created a barrier, possibly through formation of a sparingly soluble manganese-arsenate layer ($Mn_3(AsO_4)_2$), which prevented reduction of inner structural Mn(IV).

Although oxidation by Fe(III) is thermodynamically favorable, no detectable As(V) was found after 72 hours in solutions containing synthetically-prepared Fe(III) oxides at neutral pH (10,35). Therefore, Oscarson concluded that MnO_2 may be the primary component in freshwater environments responsible for decreasing the concentration of toxic As(III) through oxidative processes.

Scott and Morgan (11) found that in the presence of birnessite (pH 4 at 25°C), the depletion of As(III) was rapid and on the order of minutes with DO having no effect on the rate. Therefore they suggest 1) birnessite oxidizes As(III) through a surface mechanism, 2) adsorption of As(III) is the slowest step in the production of As(V) , and 3) oxidation products As(V) and Mn(II) are released by different mechanisms. They found that increasing pH from 4 to 8.2 had only a small effect on the rate of As(III) uptake and As(V) release. However, with increasing pH, the rate of Mn(II) release decreased. This result suggested possible formation of insoluble Mn complexes after the oxidation of As(III) at higher pH.

Oscarson et al. (12) have focused on the kinetics of As(III) oxidation in slurries containing birnessite (δ-MnO_2), cryptomelane (α-MnO_2), or pyrolusite (β-MnO_2). The oxidation for all three oxides followed first-order kinetics, with respect to the concentration of As(III), in that a plot of ln(As(III)) vs. t yielded a straight line. The rates were 0.267 h^{-1}, 0.189 h^{-1}, and 0.44 x 10^{-3} h^{-1} for birnessite, cryptomelane, and pyrolusite, respectively. The difference in rates was attributed to the crystallinity and specific surface

areas of the Mn oxides. From experiments in which mineral slurries were shaken, rate constants and energies of activation (E_A) for depletion of As(III) by the Mn oxides were determined. By comparing the calculated E_A values (26-32 kJ/mol) with typical activation energy values for diffusion (~21 kJ/mol), the authors concluded that the diffusion process was the limiting step in the process. The depletion mechanism of As(III) (oxidation + adsorption) was postulated to involve 5 steps:

1) Diffusion of As(III) to MnO_2 particle (may have to diffuse through zone of reduced Mn)
2) Sorption of As(III) to a favorable reaction site on the particle
3) Transfer of electrons from As(III) to MnO_2 forming As(V)
4) Desorption of As(V) from MnO_2 particle
5) Diffusion of adsorbed As(V) away from MnO_2 particle

The magnitude of E_A being similar in all cases suggested that the same process was limiting in all three systems. When adsorption had reached equilibrium, depletion of As(III) was still occurring; therefore, the authors postulated that in order for the concentration (As(III) + As(V)) to remain constant, a one-to-one relationship must exist between As(III) depletion and As(V) appearance in solution (i.e., oxidation followed by desorption).

In further studies, Oscarson et al. (13) investigated the effect of coating Mn oxides with Fe oxides, Al oxides, or $CaCO_3$. The rate of As(III) depletion (oxidation + adsorption) from solution was less relative to that observed with untreated Mn oxide. This behavior was attributed to a masking of electron-accepting sites as opposed to a simple dilution of the MnO_2. The reader is referred to the article for a discussion of

this behavior. The authors conclude that Fe and Al oxides and $CaCO_3$ deposited on the surface of MnO_2 profoundly affects the reactivity of MnO_2 with respect to the oxidation of As(III) and sorption of As.

Thanabalasingam (14) found the oxidation of As(III) by Mn oxides to be pH dependent. The reaction at the particle surface follows:

$$HAsO_2 + MnO_2 + 2H^+ \rightleftharpoons Mn^{2+} + H_3AsO_4$$

The effectiveness of Mn(IV) oxide as an oxidant decreased with increasing pH. At lower pH's (pH 2-5) the adsorption of As(III), which is believed to be the slow step in the oxidation (11), was fast and the oxidation products (e.g., H_3AsO_4) were adsorbed. As pH increased, less As(III) was adsorbed due to possible site-blocking reactions and as a result, oxidation did not occur to the same extent. At pH 5, the extent of adsorption of As(III) continued to decrease and As(V) was detected in solution over a limited range of initial As(III) concentration. Above this range of concentration, the possibility of forming Mn(II)-As(V) complexes, previously mentioned, increased. As pH increased to 6.5, $HAsO_4^{2-}$ was formed and greater amounts of As(V) were detected in solution due to repulsive interactions at the negative particle surface. At pH 10, the behavior resembled that at pH 5 and increased amounts of As(III) and As(V) were detected in solution. The authors postulated that formation of a Mn(II)-hydroxy species at the surface slows the adsorption-oxidation-desorption process.

Natural species which can serve as electron acceptors in the oxidation will help to detoxify arsenic. In a 13-month investigation, Knox et al. (15) found that dissolved As(III) was effectively removed at the freshwater/brackish water interface through oxidation by manganese oxides followed by adsorption on Fe-oxyhydroxide. In a study of

natural aquatic sediments, investigators (16) found that As(III) was oxidized in 48 hours in the presence of all five sediments tested. Meanwhile no oxidation was seen in the absence of sediments. To determine whether or not microbial activity was responsible for the oxidation, $HgCl_2$ was added to the systems to inhibit microbial activity. The amount of oxidation was not greatly affected. Also oxidation was not greatly affected by flushing with N_2 or air. This further proved that microbial oxidation was not key because it was very unlikely that microorganisms could have oxidized As(III) at the same rate under both aerobic and anaerobic conditions. They concluded that most natural lake sediments could oxidize As(III) through abiotic processes.

To further investigate which soil/sediment components were primary in the oxidation of arsenic, Oscarson and coworkers (17) treated freshwater lake sediments with hydroxylamine hydrochloride or sodium acetate to remove Mn. Both treatments effectively remove both Fe and Mn, but as previously mentioned, Fe(III) does not appear to be a significant oxidant of As(III). The extent of oxidation was less in treated sediments as compared to untreated sediments. The values of E_{Pt} for treated sediments were lower than those of untreated sediments, but were higher than those of untreated sediments that were flushed with N_2. No As(III) was detected in solutions slurries of the N_2-flushed, untreated sediments. Therefore, lower E_{Pt} was not correlated to the decrease in oxidation in the treated sediments..

Many natural minerals can oxidize As(III), but no As(V) was detected in slurries of illite, montmorillonite, kaolinite, vermiculite, ferruginous smectite, microline, orthoclase, or calcite within 48 hours (17). However, adsorption by these minerals may be more important.

Although it appears that MnO_2 is a primary oxidant in the geochemical environment, other species are probably more responsible in controlling soluble As concentrations. In the study of a contaminated soil, Masscheyeln and coworkers (18) studied the effect of redox potential (E_{Pt}) and pH on As speciation and solubility. At higher soil redox levels (500-200 mV) arsenic solubility was low and the major species present was As(V). An alkaline pH (pH 8) coupled with reduction of As(V) to As(III) resulted in increased amounts of arsenic in solution. Soluble arsenic increased 13-fold at lower redox levels (-200 mV). Soluble arsenic was also found to be controlled by dissolution of the Fe phase.

Two experiments were performed in the study mentioned above (18). The first experiment involved a time/depth evaluation of E_{Pt}, pH, soluble Fe and Mn species, and soluble arsenic species within an arsenic contaminated soil under flooded conditions. Between the 1st and 3rd days, soluble arsenic concentrations doubled with As(III) becoming the dominate species. The increase was attributed to reduction of As(V) and subsequent release of As(III). After 3 days of flooding, soluble Mn increased. When E_{Pt} dropped to <150 mV, soluble Mn reached a near constant level. The reduction of Mn(IV) to the more soluble Mn(II) did not correlate with an oxidation of As(III) because As(III) remained the predominant arsenic species in solution. In contrast, no Fe was detected in solution until between the 15th and 35th day when redox levels dropped below 100 mV. Data showed a sharp and correlative increase of total soluble As and Fe. As(V) was believed to be coprecipitated with the iron oxyhydroxide (molar ratio of 0.8-1.7) and released upon Fe-oxyhydroxide solubilization. Because of the considerable amount of As(V) still present under reducing conditions, the authors postulated that As(V) was

released and slowly reduced. The reduction was thought to be slow because of the competition between Fe(III) and As(V) as electron acceptors in microbial respiration.

In the second experiment under *controlled* E_{Pt} and pH, both parameters were again found to affect arsenic speciation and solubility. For E_{Pt} values of 200 and 500 mV, As(V) was predominant, but when E_{Pt} was lowered to 0 and -200 mV, As(III) became predominant and the soluble arsenic concentration increased. Data showed that abiotic oxidation by MnO_2 of As(III) was not important because As(III) remained predominate even after soluble Mn reached a maximum after 3 days in the 24-day equilibration. Increases in the soluble arsenic concentration were believed to be a result of As(V) reduction and Fe-oxyhydroxide solubilization.

Under oxidizing conditions at alkaline pH, the amount of soluble arsenic increased as much as 3 times as compared to more acidic pH and oxidizing conditions. At higher pH's and under oxidizing conditions, most of the soluble arsenic was present as As(V). This increase in total soluble As was attributed to the pH-dependent adsorption characteristics of As(V) on oxide surfaces (10,13,19). Increasing pH decreases the positive surface charge and facilitates desorption of As(V). As more reducing conditions were reached, As(III) became dominant. However, total soluble arsenic decreased at alkaline conditions as compared to more acidic conditions. The reason for this behavior was unclear, but it was speculated that slower dissolution of Fe-oxyhydroxide under alkaline conditions could result in the decrease in total soluble As. Additionally, the presence of soluble organics and the formation of iron oxyhydroxide-organic matter complexes at alkaline pH could retard the reduction of the Fe phase.

Masscheylen et al. summarized their results as follows:

- both microbial and chemical oxidation of As(III) are possibly occurring
- reduction of As(V) to As(III) was correlated with reduction of the Mn phase
- reduction of As(V) and dissolution of Fe-oxyhydroxide increases soluble arsenic concentrations

Crecelius et al. (1) have suggested, based upon the following evidence, that in most natural waters, arsenic redox species may not occur in thermodynamic equilibrium but more likely may exist in a quasi-steady state. Cherry et al. (20) observed that in deoxygenated waters, the initial ratio of 1 for As(III)/As(V) remained unchanged for 78 days over a pH range of 2 to 10.5. Studies involving naturally occurring redox agents (i.e., Fe(III), H_2, H_2S, O_2, $H_2PO_2^-$) indicated that oxidation or reduction of arsenic by these agents at natural concentrations would take months or years. It is probable that in natural waters containing small amounts of redox agents, the chemical oxidation or reduction of As would reach equilibrium over very long time scales. Nonetheless, they proposed that in the absence of thermodynamic equilibrium, the ratio of As(III) to As(V) may be indicative of the apparent redox level. To be useful the oxidation of As(III) or reduction of As(V) would have to be rapid relative to biogeochemical processes controlling the redox level but slow enough to permit sample collection and analysis.

In contrast, Stauffer et al. (37) observed that in hot spring drainages, that although total dissolved arsenic was approximately constant, the As(III) to As(V) ratio was bimodal depending the on the S^{2-} concentration. In contrast to these findings, the authors found that the As(III)/As(V) ratio remained constant within an oxygenated flowing river and through the reservoir into which the river flowed.

Conclusions concerning the redox behavior of arsenic are as follows:

- the redox behavior of arsenic depends on its adsorption characteristics
- the principal control on the distribution and speciation of aqueous arsenic are system E_{Pt} and pH
- under most environmental conditions (E_{Pt} -200 to 400 mV and pH 5 - 9), As(V) will be present as the $H_2AsO_4^-$ or $HAsO_4^{2-}$ species; As(III) will be present as the H_2AsO_3 species
- manganese oxides have the potential to oxidize arsenic abiotically with the potential being dependent on mineral structure and pH
- thermodynamic equilibrium between As(III) and As(V) may not exist but rather a quasi-steady state may be achieved

Adsorption/Desorption/Solubilization/Precipitation

As can be seen above , the redox behavior of arsenic is highly dependent on its adsorption characteristics. Adsorption of arsenic is believed to occur through specific adsorption as opposed to purely electrostatic adsorption (19). Specific adsorption is a combination of ionic and non-ionic bonding interactions which can occur even at negatively-charged surfaces. Models based on heterogenous surface sites as opposed to homogenous surface sites also tend to explain the adsorptive behavior more adequately (5,19,21).

All of the arsenicals (As(V), As(III), MMAA, DMAA) form very insoluble species in soils by interactions with hydrous oxide coatings on clay particles. Adsorbents of arsenic

include Fe and Al hydrous oxides and clays. Bauxite, silicates, and carbonates show only moderate adsorption. Lum and Edgar (22) found that in sediment core samples that Mn/Fe oxides, organic matter/sulfides, and carbonates were the important solid phases binding arsenic. Shnyukov (23) observed that iron ores are enriched with arsenic because of the high adsorptive capacity of hydrous iron oxides. Adsorption is found to be proportional to pH, clay type, and iron content.

Frost and Griffin (24) presented the following simple reaction for the adsorption of arsenate ($H_2AsO_4^-$):

$$>M-OH + H_2AsO_4^- \Longrightarrow >M-H_2AsO_4 + OH^-$$

A surface site on the hydrous oxide or clay is originally occupied by an anion such as OH^-. Arsenate is then adsorbed through exchange with the hydroxyl or some other adsorbed anion.

In aerobic environments, arsenate predominates and can, as indicated earlier, coprecipitate with iron hydroxides (18). Arsenate is similar to phosphate and may be isomorphously substituted in phosphate minerals (1). In general, soils high in phosphate do not adsorb as much arsenic compared to soils low in phosphate. Stowe (36) found that in Florida phosphate pebbles, the arsenic content increased with the increasing iron content and decreased with increasing phosphate content, indicating the affinity of arsenic for iron. Arsenite and arsenious acid species also adsorb or coprecipitate with iron oxides. The arsenite adsorption capacity was found to be correlated with the Fe oxide content of five West Virginia soils (26, 27). As(III) has a strong affinity for sulfide and readily adsorbs or coprecipitates as metal sulfides. Orpiment (As_2S_3) is believed to provide a solubility control for arsenic (1).

Arsenate and arsenite differ in their adsorption properties and this influences mobilization and distributions. Rates and extent of adsorption depend on the type of adsorbent, initial arsenic concentration, and pH. In general, arsenic is predominately adsorbed as the As(V) species (1,7,10,19,21). Rates and extent of arsenate removal are generally greater than those for arsenite (19,21). Gupta and Chen (21) found the rate and extent of As(V) adsorption to be greater than those of As(III) on activated alumina and bauxite. Adsorptive behavior adhered to the Langmuir equation. The percent of As(V) added which was adsorbed was 50% and 40% on activated alumina and bauxite as compared to 6% and 2% for As(III). In the pH range 4 to 7, As(V) was effectively removed with adsorption decreasing with increasing pH. As(III) adsorption was nearly constant between pH 4 and 9 but dropped off sharply at pH greater than 9. The effect of initial arsenic concentration was also greater for As(III). Percent removal decreased with increasing initial As(III) concentration. The adsorptive behavior of arsenic depends on the anion adsorption characteristics of the adsorbent material. If electrostatic and specific adsorption mechanisms are both at work, points of inflection should result at or near pK values of the species being adsorbed (28). Indeed, inflections were apparent at pH 7 and 9 for As(V) and As(III), respectively.

Pierce and Moore (19) studied the adsorption characteristics of arsenic on amorphous iron hydroxide (pH_{iep} = 8) over various concentrations and pH's. The pH_{iep} is the pH at which the surface charge of the adsorbent is neutral. The rate of adsorption of As(III) was found to be fast, reaching 90% completion after 2 hours. However, As(V) adsorption had reached 90% completion after only 1 hour. In general, more arsenate was adsorbed (up to 1.5mmol/g adsorbent) as compared to arsenite (up to 0.5 mmol/g adsorbent). The rate of

adsorption increased with increasing initial As(III) concentration, but only slight variations in the rate were noticed with increasing As(V) concentration. Although the rate of adsorption increased with increasing initial As(III) concentration, the percent of As(III) adsorbed decreased. Because the time scale of adsorption was on the order of hours and shifts in pH_{iep} were observed, they suggested that there was a specific interaction rather than a simple electrostatic interaction between arsenic and the adsorbent.

The greater adsorption of arsenate at a given pH was attributed to the differing pK_a's and resulting charge of the adsorbent. Arsenate is negatively charged over a wide pH range whereas arsenite is neutral up to about pH 9 and then is negatively charged. Arsenate displayed maximum adsorption at pH 4 while arsenite had a maximum adsorption at pH 7. Arsenic acid has pK_a's of 2.2, 6.9, and 11.5 and thus would have been present as $H_2AsO_4^-$ and $HAsO_4^{2-}$. These species would have a greater effect on the surface charge than arsenious acid which has a pK_a of 9.2 and would have been present as $H_2AsO_3^-$ and H_3AsO_3. Indeed, larger shifts in the pH_{iep} were observed for arsenate (pH_{iep} 8 $\rightarrow$ 4.7) as compared to arsenite (pH_{iep} 8 $\rightarrow$ 7.3).

The pH also affects the surface of the oxide. As pH increases, the surface becomes less positive and adsorption decreases. The authors conclude that adsorption of arsenic onto Fe oxides is best explained by a heterogenous site model. The observation of two different isotherms is postulated to be due to different types of binding sites on the surface of the oxide.

Frost and Griffin (24) studied the adsorption of As(V) and As(III) from a landfill leachate on the clay minerals montmorillonite and kaolinite. Arsenate adsorption increased up to pH 4, exhibited a peak between 4 and 6, and then decreased on both

kaolinite and montmorillonite. Arsenite adsorption increased steadily from pH 4 to 9 on kaolinite but displayed a maximum near pH 7 on montmorillonite. Both minerals adsorbed lesser amounts arsenite. Montmorillonite tended to adsorb As(V) and As(III) more strongly than kaolinite.

The adsorptive behavior of manganese oxides differs from most other minerals in that the surface is negatively charged in the natural pH range. Investigators (14) studying the effect of adsorption of As(III) on manganese oxides found the maximum uptake occurred at pH < 5. For pH > 5 sorption declined because increasing amounts of the oxidation product (As(V)) existed as the negatively-charged species. A repulsion of this species at the surface accounts for the drop in adsorption.

The isomorphs of manganese oxide differ in the extent of adsorption of arsenic with the order being cryptomelane > birnessite > pyrolusite (12). The adsorption is dependent on the specific surface and surface charge. At neutral pH, As(III) is uncharged and therefore surface charge is unimportant. However, the adsorption of As(V), which is negatively charged at pH 7, depends on the PZC (point of zero charge) of the oxide surface. The PZC values of birnessite, cryptomelane, pyrolusite are 2.3, 2.8, and 6.4, respectively. Therefore, birnessite and cryptomelane have a net negative surface charge in the natural pH range while that of pyrolusite is only slightly negative. When arsenic is added as As(III), some is inevitably oxidized to As(V) which becomes adsorbed. The authors speculated that there is no energy barrier from charge repulsion to overcome because As(V) is produced at the surface of the oxide as opposed to being adsorbed from solution. Because As(V) is negatively charged at pH 7 and birnessite has a greater charge density then cyrptomelane, the repulsive interaction is stronger for birnessite and therefore the

amount of As sorbed is less overall. This same rational can be applied to adsorption of As(III) on birnessite. Pyrolusite adsorbs less As(III) and As(V) because of its smaller surface area.

Anderson et al. (29) studied the adsorption of arsenate exclusively on amorphous aluminum hydroxide. They found an empirical correlation between pH_{iep} and amount of arsenate adsorbed at the IEP (Γ_{iep} (μmole/g)) which could be used to describe anionic adsorption of arsenate. Experimentally they found that 90% of the adsorption took place before a sample could be collected indicating an incredible rate of adsorption for Al oxide. In general, arsenate adsorption was independent of pH at low pH. The extent of adsorption tended to decrease with increasing pH; however, it generally increased with increasing initial arsenate concentration. The pH at which the amount of As(V) adsorbed began to decrease was a function of the initial arsenate concentration.

The pH_{iep} was found to be a function of initial As(V) concentration, decreasing from 8.5 with no arsenate, to 4.6 for concentrations greater than 800 μM. From a plot of adsorption at the IEP vs. pH_{iep}, Γ_{iep} was seen to be a linear function of pH between pH 8.5 and pH 4.6. With increasing amounts of adsorbed arsenate, the surface potential of the Al hydroxide became more negative, and the pH at which this surface becomes neutrally charged shifted to lower values. The authors conclude that, in general, when the quantity $pH - pH_{iep}$ is less than zero, the surface of the hydroxide is positive and adsorption is at a maximum corresponding to Γ_{iep}. When $pH - pH_{iep}$ is greater than zero, the surface is negatively charged and the amount of As(V) adsorbed will decrease because of electrostatic repulsion. At higher pH, adsorption was attributed to specific interactions at the oxide surface.

Goldberg (30) used a surface complexation/constant capacitance model to fit adsorption data for arsenate on Al and Fe oxide minerals. The model describes adsorption as a ligand exchange mechanism. Arsenate adsorption was believed to occur through exchange with surface hydroxyl or aquo groups (26,29). The model defines possible surface complexes and reactions and quantitatively described arsenate adsorption on goethite, gibbsite, and amorphous Al hydroxide.

Up to this point, adsorption of arsenic species at synthetic surfaces has been discussed. The natural adsorptive behavior, like the natural redox behavior, could vary significantly. Competing ions undoubtedly play a crucial role in arsenic adsorption.

Unless surfaces are coated with natural organic matter, the surface charge of Fe and Al oxides is often positive in geological environments as opposed to that of Mn oxides which are often negative (25). Thus, uncoated iron oxides adsorb negatively-charged arsenic species preferentially compared to manganese oxides. Coprecipitation with Mn/Fe oxides can control dissolved arsenic concentration in waters. Peterson et al. (31) found that arsenic concentrations in pore water are correlated with Fe(II) concentration rather than Mn(II) suggesting that release of arsenic was closely associated with dissolution of iron oxyhydroxide. It was postulated that even if large quantities of arsenic were adsorbed by the Mn phase, Mn (IV) would be reduced and dissolved before Fe(III), and therefore, any arsenic released during this process would be re-adsorbed by the Fe phase. Ultimate release of arsenic is thus controlled by the Fe phase.

Edenborn et al. (32) found that at the 3-cm oxidized zone of a sediment core, E_{Pt} was characterized as positive to slightly negative with lower concentrations of Mn(II), Fe(II), and arsenic. At the 4-cm level, bacterial sulfate reduction began and the E_{Pt} decreased.

With this decrease, concentrations of dissolved Mn, Fe, and arsenic increased. In further experiments, it was shown that Mn dissolved at a higher E_{Pt} and the release of arsenic was simultaneous with that of Fe. The release of arsenic and Fe occurred at the redox potential characteristic of organic matter degradation (-100 to +100 mV). It was suggested that sulfate reduction was necessary to maintain the reducing conditions conducive to iron dissolution.

Andreae (2) suggested that arsenic is released to sediment pore waters upon Mn/Fe dissolution or degradation of organic matter. The balance between addition to and removal from pore water differed for As(V) and As(III). Arsenate displayed a flux from water to sediments while As(III) displayed a flux from sediments to water.

Gulens (7) found that the extent of adsorption in elution experiments with sand columns varied with the oxidation state of arsenic, the redox environment, and/or the pH of the eluting water. In oxidizing environments, As(III) eluted faster and in greater quantities than As(V). Under reducing conditions, both eluted similarly. The faster elution of As(III) was taken as an indicator of the weaker interaction between Fe(III) minerals and As(III) as compared to the interaction between the same minerals and As(V). For more reducing conditions, the As(V) mobility increased because the pH of the eluting water increased (change in surface charge of adsorbent) or because of the reduction of Fe(III) minerals to Fe(II) resulting in solubilization of the iron phase.

In a study of arsenate adsorption by a calcareous, montmorillonitic soil, Goldberg (33) found adsorption increased with increasing pH, exhibited a peak near pH 10.5, and decreased at higher pH. For the reference materials montmorillonite and kaolinite, adsorption exhibited a peak near pH 5 and decreased with increasing pH. The extent of

arsenate adsorption was found to be similar for both clays. For the reference material calcite, adsorption increased from pH 6 to 10, peaked between 10 and 12, and decreased with increasing pH. The extent of adsorption on calcite was 4 times that for kaolinite and montmorillonite.

The authors used the constant capacitance model to describe arsenate adsorption on both the soil and the two clays. The model fit the soil adsorption behavior up to pH 9 but could not fit the peak at 10.5. The poor fit at higher pH was attributed to the presence of more than one type of adsorption site on the material. The authors concluded that for this soil, adsorption was controlled by kaolinite and montmorillonite below pH 9 and was controlled by calcite above pH 9.

Adsorptive competition from other ions in solution affects the uptake of arsenic in soils. Investigators (34) observed similar absorption maxima for both phosphorus and arsenic on goethite over the pH range 3-13. Hydrous alumina adsorbed similar amounts of both arsenic and P in dilute solutions, but adsorbed more arsenic in more concentrated solutions of the two species. On the other hand, soil samples were observed to adsorb more P than arsenic when saturated with both anions separately and alternately. Phosphorous and arsenic are also known to displace each other from adsorptive sites (28).

Conclusions concerning the adsorptive behavior of arsenic are as follows:

- As(V) is found to adsorb faster and more extensively than As(III)
- Fe/Al oxides and clays display greater adsorptive ability compared to Mn oxides
- Arsenic can be soluble and mobile regardless of its oxidation state

- Adsorption of arsenic species is believed to occur mainly through specific adsorption processes
- Surface charge, surface area, and pH are key in the adsorptive behavior of arsenic

Biological Methylation

Organoarsenic compounds are widely distributed and have been detected in aquatic systems, the atmosphere, soils and sediments, and biological tissue (9). Certain fungi, yeasts, and bacteria are known to methylate arsenic (25). The methylation process can transform inorganic arsenic species to the more toxic methyl arsines. Dimethylarsinic acid (DMAA) is a major form of arsenic in the environment. It is involved in biological systems and highly resistant to oxidation. Monomethylarsonic acid (MMAA) species are generally found in lower concentrations. To date, MMAA and DMAA are the only organoarsenicals which have been detected in natural waters (9). Ferguson and Gavis (25) speculate that methylation of arsenic by organisms may not only be a detoxification process but also a process, in anaerobic environments, which is energetically favorable compared to synthesis. Cullen and Reimer (9) is an excellent source on the various methylating processes and the organisms that are responsible for these transformations.

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Appendix B

E_H - pH Diagram

Figure B.1 is an E_H - pH diagram for the As-Fe-S-H_2O system. This diagram is similar to that shown in Figure 2.1. However, this diagram includes the additional sulfidic mineral phase of arsenopyrite. As can be seen from the diagram, this mineral will be unstable at an E_H above -300 mV and will subsequently undergo oxidative dissolution thereby "freeing" the elemental As. The elemental As can then subsequently be oxidized to either As(III) or As(V).

The diagram was generated with the program entitled HSC Chemistry for Windows from Outokumpu Research. Table B.1 lists the various species, with free energies of formation, used to generate the diagram. An arsenic concentration of 1×10^{-2} mol/kg was used because this approximates the average concentration of arsenic found in the tailing material at Sutter Creek, Ca.

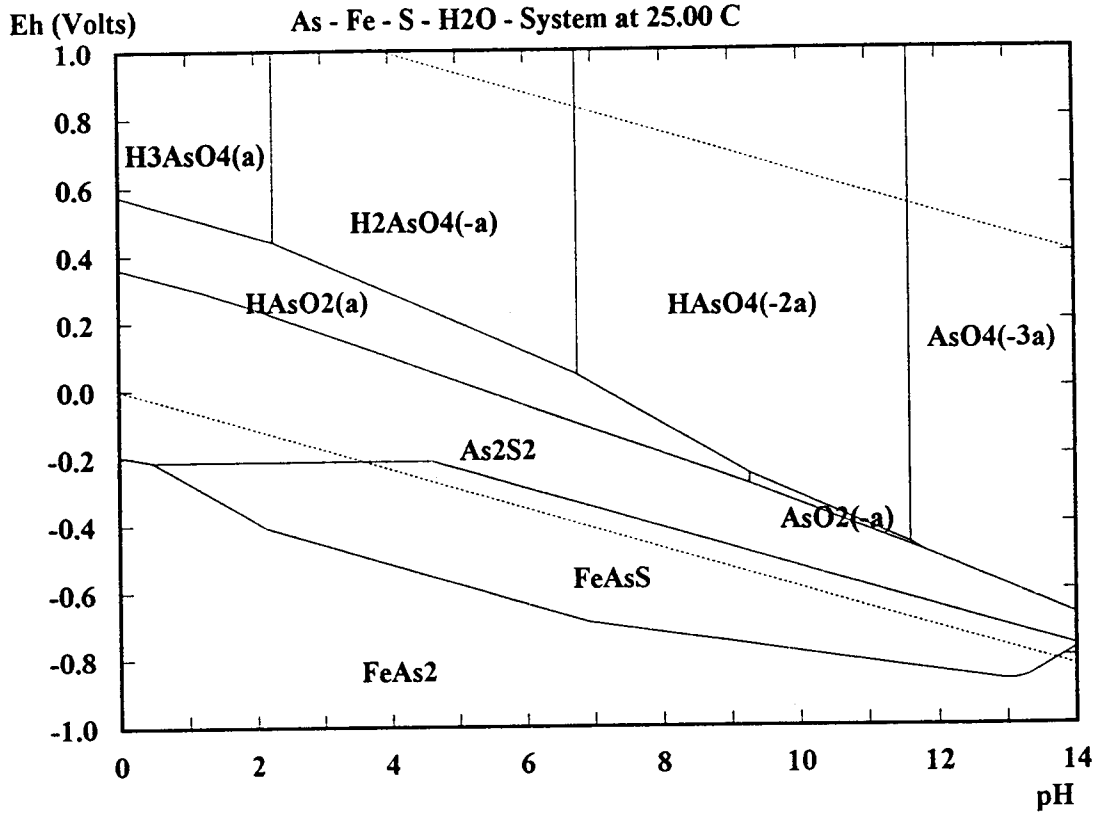

Figure B.1 E_H - pH diagram for the As-Fe-S system.

Table B.1 Species used in Development of Figure B.1

Temperature	=	25.000	C
Delta G of H20	=	-56.678	kcal/mol
Dielectric Constant	=	78.384	
Ion Strenght	=	0.000	

pH min	V min	pH max	V max
0.000	-1.000	14.000	1.000

Element	Molality	Pressure
Fe	1.000E+00	1.000E+00
S	1.000E+00	1.000E+00
As	1.000E-02	1.000E+00

Species	Delta G kcal/mol
Fe	0.000
Fe0.9470	-58.027
FeO	-60.096
Fe2O3	-177.716
Fe3O4	-242.666
Fe(OH)2	-117.587
Fe(OH)3	-168.614
Fe2O3*H2O	-233.230
Fe(+3a)	-1.101
Fe(+2a)	-18.853
FeO2(-2a)	-44.715
Fe(OH)3(a)	-119.760
FeOH(+2a)	-54.794
FeOH(+a)	-66.291
Fe(OH)2(+a)	-83.481
Fe(OH)3(-a)	-104.484
Fe(OH)4(-2a)	-124.863
Fe2(OH)2(+4a)	-111.743
HFeO2(-a)	-64.405
H2S2	-4.765
H2SO4	-164.908
H2SO4*6.5H2O	-546.292
H2SO4*H2O	-227.137
H2SO4*2H2O	-286.714
H2SO4*3H2O	-345.112
H2SO4*4H2O	558.456
S	0.000
H2S(a)	-6.529
HS(-a)	2.899
H2SO3(a)	-128.565
H2SO4(a)	-177.960
H2S2O4(a)	-104.297
H2S2O8(a)	-266.512
HSO3(-a)	-126.133
HSO4(-a)	-180.671
HS2O4(-a)	-103.797
S(-2a)	20.535
S2(-2a)	19.015
S3(-2a)	17.607
S4(-2a)	16.538
S5(-2a)	15.741
SO2(a)	-71.848
SO3(a)	-125.644
SO4(-2a)	-177.960
S2O3(-2a)	-124.003
S2O4(-2a)	-143.573
S2O8(-2a)	-266.512
S4O6(-2a)	-248.711
As	0.000
As2O3(A)	-137.723
As2O3	-137.678
As2O4	-167.528
As2O5	-186.948
As2S2	-33.422
As2S3	-18.844
As4S4	-31.079
FeAs2	-12.497
FeAsS	-25.784
AsO(+a)	-33.963
AsO2(-a)	-83.633
AsO4(-3a)	-154.959
HAsO2(a)	-96.282
H3AsO3(a)	-152.876
H3AsO4(a)	-183.103
HAsO4(-2a)	-170.788
H2AsO3(-a)	-140.304
H2AsO4(-a)	-180.020